

Green Synthesis of Silver Nanoparticles Using *Hibiscus sabdariffa* Leaves Extract

Siti Husnaa Mohd Taib, Kamyar Shameli*, Roshafima Rasit Ali, Zahra Izadiyan and Zatil Izzah Ahmad Tarmizi

Department of Environment and Green Technology, Malaysia-Japan International Institute of Technology, Universiti Teknologi Malaysia, Jalan Sultan Yahya Petra, 54100 Kuala Lumpur, Malaysia

* Correspondence: kamyarshameli@gmail.com; Tel.: +6017 344 3492

<https://doi.org/10.37934/jrnn.3.1.7681>

ABSTRACT

The present paper reports the synthesis of silver nanoparticles (Ag-NPs) by a green method using *Hibiscus sabdariffa* (*H. sabdariffa*) leaves extract as reductant and stabilizer. The synthesized Ag-NPs were characterized by ultraviolet-visible (UV-vis) spectroscopy, transmission electron microscopy (TEM), atomic force microscopy (AFM) and Fourier transform infrared spectroscopy (FTIR). UV-vis spectrum of synthesized Ag-NPs showed a peak at 378 nm. TEM analysis revealed that the particles were spherical and irregular in shape and has average size around 56.52 nm. This structure and size of particles were confirmed by AFM analysis. The UV-vis and FTIR spectrum provides evidence of the presence of caffeic acid component as a representative biomolecule in stabilising the nanoparticles based on previous studies. Hence, this study advocates that *H. sabdariffa* have potential for synthesizing nanoparticles.

Keywords:

Green synthesis, silver nanoparticles, *Hibiscus sabdariffa*, AFM, TEM.

Received: 28 May 2021

Revised: 22 June 2021

Accepted: 29 June 2021

Published: 7 August 2021

1. Introduction

Nanoparticles (NPs) are a particle that is not in bulk samples of the same material with sizes between 1 to 100 nm [1]. The synthesis and characterization of noble metal NPs such as silver (Ag), gold (Au) and platinum (Pt) is an emerging field of research due to their important applications in the fields of biotechnology, bioengineering, textile engineering, water treatment, metal-based consumer products and other areas [2]. Ag-NPs have been widely studied and have many applications. Since ancient times, Ag metals have been reported that it is known to have antimicrobial activities and Ag-NPs are of particular interest due to their peculiar properties and wide applications [3]. Meanwhile, Ag-NPs have been reported as a good electro-catalyst candidate of nanocomposite for oxygen reduction reaction in alkaline fuel cell [4].

1 Many methods have been used for the synthesis of Ag-NPs, like sonochemical [5], electrochemical
2 techniques [6], chemical reduction and radiolysis methods [7]. Currently, green method for the
3 synthesis of NPs is growing into a vital branch of nanotechnology, because these methods are
4 considered safe and cost effective as an alternative to conventional methods.

5 One of the herb plants that was found to have a good value is *Hibiscus sabdariffa* (*H. sabdariffa*)
6 which can act simultaneously as reducing and stabilising agents in synthesizing Ag-NPs because this
7 plant is well-known in produces an excellent source of antioxidant compounds. In Malaysia, *H.*
8 *sabdariffa* that commonly known as roselle was cultivated for use as a drink and food. It is also known
9 locally as asam susur, asam paya or Ribena Malaysia, and closely resembles cranberries in flavour
10 [8]. It is also used as native medicine in Africa, India and Mexico. The plant extract of leaf and calyx
11 found to be antibacterial, diuretic effect, antioxidant, anti-diabetic, anti-cholesterol, chemo-protective,
12 anti-hypertensive, blood pressure suppressive, anti-tumour and anti-cancer agent [9]. Chen et al., in
13 2013 have reported that the total flavonoid content in extract of *H. sabdariffa* leaves was estimated to
14 be about 75.0% that represented a possible source of greater polyphenolic compounds, which could
15 be responsible for the antioxidant capacity compared to the calyces that only to be around 20.2% [10].
16 Additionally, Wang et al., in 2014 reported that neochlorogenic acid, chlorogenic acid,
17 cryptochlorogenic acid, rutin and isoquercitrin were the major phenolic and flavonoid in *H. sabdariffa*
18 leaves [11].

19 In the present work is dedicated to the use of *H. sabdariffa* leaves extract as reducing agent in
20 synthesized Ag-NPs. The characterization of synthesized Ag-NPs was done using ultraviolet-visible
21 (UV-vis) spectroscopy, transmission electron microscopy (TEM), atomic force microscopy (AFM) and
22 Fourier transform infrared spectroscopy (FTIR).

23 24 **2. Materials and Methods**

25 *2.1. Materials*

26
27 Silver nitrate (AgNO_3) was analytical grade (99.89%) from Bendosen Laboratory Chemicals,
28 Selangor, Malaysia. The fresh leaves of *H. sabdariffa* leaves were obtained from Batu Pahat, Johor.
29 Sodium hydroxide (NaOH) was purchased from R&M Chemicals. All the chemicals were used
30 without further purification for this research.

31 32 *2.2. Synthesis of Ag-NPs*

33
34 Ag-NPs were synthesized at room temperature from AgNO_3 solution using the *H. sabdariffa* leaf
35 extract. Briefly, 5 ml (5 mM) aqueous solution of AgNO_3 was added to 20 ml of 5 mg/ml *H. sabdariffa*
36 leaves extract and stirred for 5 min. The solution turned yellowish brown upon stirring. Then, 0.8 ml
37 of 1M NaOH was added to the solution and stirred for another 5 min. The solution turned to dark
38 brown colour.

39 40 *2.3. Characterization of Ag-NPs*

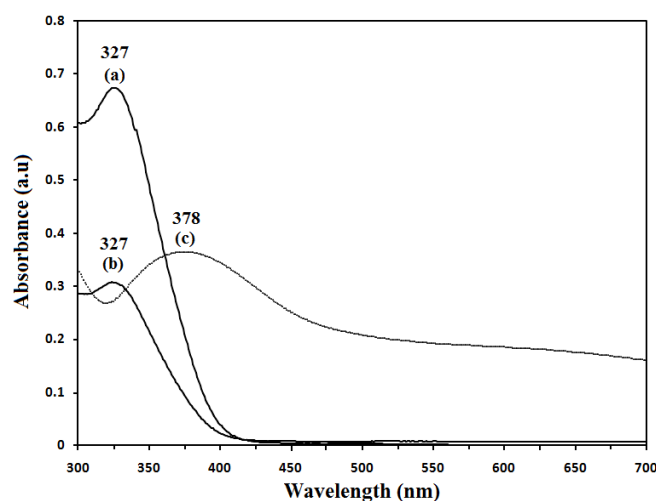
41
42 UV-vis spectra of the synthesized Ag-NPs were recorded using UV-vis spectrophotometer (UV-
43 1800, SHIMADZU) in the 200-800 nm wavelength range. Shape and particle size distribution of
44 synthesized Ag-NPs solution was analysed by Hitachi H-7100 TEM (100 kV). To further characterize
45 the size and dispersion of the Ag-NPs, the colloidal solution was dried as a thin layer on mica-based
46 glass slide and then was visualized using AFM, model Bruker AXS, CA, USA. FTIR spectra were

1 recorded using a KBr pellet technique with a Thermo Scientific Nicolet 6700 FTIR spectrometer in the
2 range of wavenumbers 400 to 4000 cm^{-1} .

3. Results and Discussion

3.1. UV-vis spectra analysis

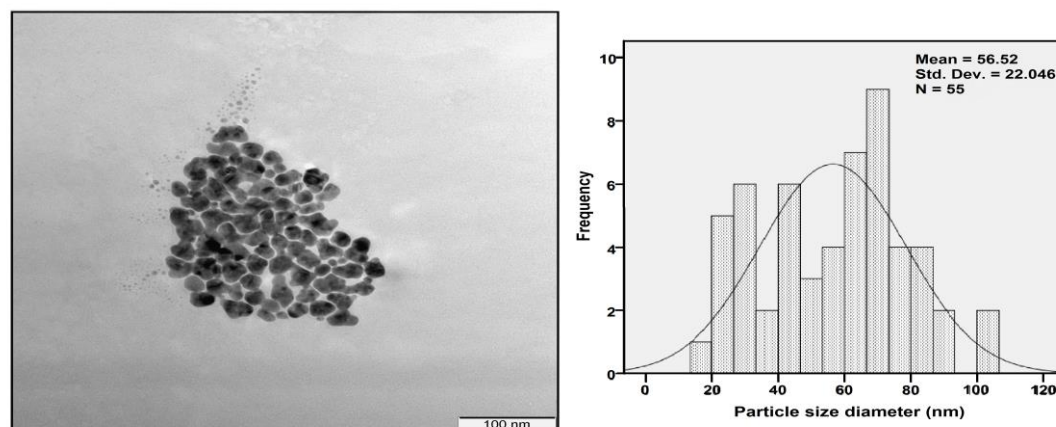
7 To confirm the formation of Ag-NPs, the absorption band characteristics were observed as
8 reported in Figure 1. *H. sabdariffa* leaves extract shows an absorption peak at 327 nm due to the
9 presence caffeic acid compounds [12]. The addition of AgNO_3 solution to *H. sabdariffa* leaves extract
10 does not cause any alteration in the peak position of the absorption spectrum at 327 nm, but only a
11 reduction of intensity due to dilution. Thus, a mixture of *H. sabdariffa* leaves extract and AgNO_3 is
12 indefinitely stable and no reactions occur. However, the addition of NaOH turning the pH alkaline,
13 start an immediate reaction: Ag^+ is reduced into metallic NPs as suggested by the new peak in the
14 spectrum at 378 nm is due to surface plasmon resonance. The caffeic acid band of *H. sabdariffa* leaf
15 extract originally located at 327 nm disappeared completely. This is due either to the oxidation of
16 caffeic acid, which have permitted the reduction of Ag^+ ions, or to the shift of this band in alkaline
17 solutions toward 378 nm. In alkaline solution the caffeic acid of *H. sabdariffa* leaf extract is unstable
18 and undergo a rapid oxidation reaction at the expenses of the Ag^+ ions or the oxygen from the air.
19 The resulting colloidal Ag solution is indefinitely stable since the *H. sabdariffa* leaves extract
20 components act as reducing and stabilising agents.



21
22 **Figure 1.** UV-vis absorption spectra for (a) *H. sabdariffa* leaves extract (b) with addition of AgNO_3 solution (c)
23 formation of Ag-NPs after the addition of NaOH.

3.2. TEM analysis

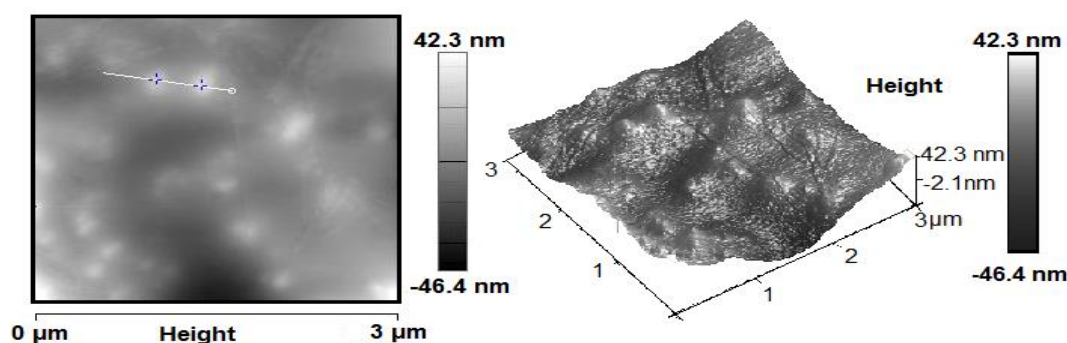
27 TEM image of the Ag-NPs is depicted in Figure 2. The shape of the synthesized Ag-NPs was
28 spherical and irregular in shape. The histogram represents the size distribution of the synthesized
29 Ag-NPs, which have an average size of the particles of 56.52 ± 22.046 nm (Figure 2). The number of
30 Ag-NPs counts was around 55.



1
2 **Figure 2.** TEM images and histogram plots that showing the particle size distribution of Ag-NPs.

3
4 **3.3. AFM analysis**

5
6 The AFM results displayed the surface morphology of the synthesized Ag-NPs (Figure 3). The
7 particle size of the synthesized Ag-NPs was in the average around 51.32 nm. The topographical image
8 of Ag-NPs in particular bright spots indicated that they are formed NPs mostly spherical in shape
9 which match with TEM analysis.

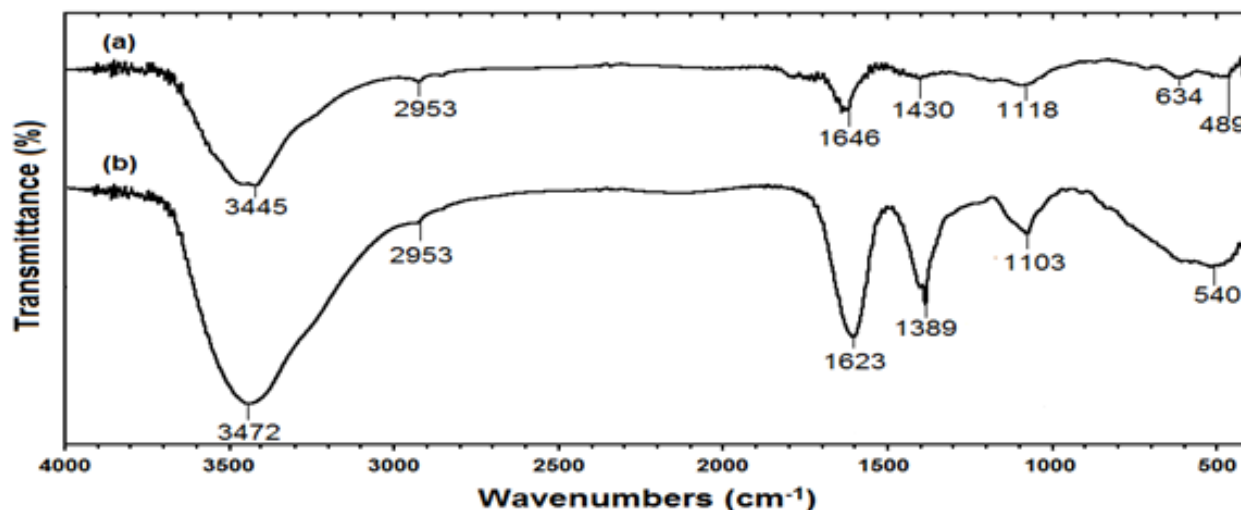


10
11 **Figure 3.** AFM topography of synthesized Ag-NPs by *H. sabdariffa* leaves extract.

12
13 **3.4. AFM analysis**

14
15 FTIR analysis was done to identify the possible biomolecules present in *H. sabdariffa* leaves extract
16 responsible for efficient stabilization of the Ag-NPs. The comparative FTIR profile of *H. sabdariffa*
17 leaves extract and the synthesized Ag-NPs, is depicted in Figure 4. In *H. sabdariffa* leaves extract, the
18 absorption peak was observed at 3445 cm⁻¹, 2953 cm⁻¹, 1646 cm⁻¹, 1430 cm⁻¹, 1118 cm⁻¹, which are
19 associated -OH stretching, -CH stretching, C=C aromatic stretch, -OH bending, and -C-OH stretch
20 respectively. Whereas, the lower frequency band at 634 cm⁻¹, and 489 cm⁻¹ were noticed to be the in-
21 plane bending modes of the carbonyl group [13]. These entire peaks related to the caffeic acid
22 components that presence in *H. sabdariffa* leaf extract which were covenant with previous literatures

1 [12,14]. The peak at 3445 cm^{-1} in *H. sabdariffa* leaves extract represents the stretching vibration -OH
2 group that attached to the aromatic ring structures of flavonoids compound [15] was shifted to 3472 cm^{-1}
3 cm^{-1} in synthesized Ag-NPs spectrum which indicated that -OH functional group was likely involved
4 in the synthesis of Ag-NPs. Almost similar FTIR spectra were observed for both the plant extract and
5 the formation of the Ag-NPs indicated that the Ag-NPs were effectively coated by the caffeic acid
6 present in *H. sabdariffa* leaves extract.



7
8 **Figure 4.** FTIR spectra of (a) *H. sabdariffa* leaves extract and (b) synthesized Ag-NPs.

9 10 **4. Conclusions**

11 In conclusion, we report a simple green synthesis route for preparing Ag-NPs using *H. sabdariffa*
12 leaf extract as a reducing and stabilizing agent. The characterization study of UV-vis, TEM, AFM and
13 FTIR analysis evidenced the formation of Ag-NPs. This study provides baseline information for the
14 synthesis of NPs from plant sources of *H. sabdariffa* leaves and need for further exploration of their
15 potent novel applications.

16 17 **Funding**

18 This research was funded by the Ministry of education under FRGS grant, Universiti Teknologi
19 Malaysia (UTM), project number PY/2015/05547 and Malaysia-Japan International Institute of
20 Technology (MJIIT).

21 22 **Acknowledgement**

23 The authors thank colleagues and collaborators who have contributed to the development of this
24 work.

25 26 **References**

- 27 1. Auffan, M.; Rose, J.; Bottero, J-Y.; Lowry, G.V; Jolivet J-P.; Wiesner, M.R. Towards a definition of
28 inorganic nanoparticles from an environmental, health and safety perspective. *Nat. Nanotechnol.* 2009,
29 4, 634-41.

- 1 2. Padalia, H.; Moteriya, P.; Chandra, S. Green synthesis of silver nanoparticles from marigold flower and
2 its synergistic antimicrobial potential. Arab. J. Chem. 2015, 8, 732–41.
- 3 3. Pal, S.; Tak, Y.K.; Song, J.M. Does the antibacterial activity of silver nanoparticles depend on the shape
4 of the nanoparticle? A study of the gram-negative bacterium *Escherichia coli*. Appl. Environ. Microbiol.
5 2007, 290, 1712–20.
- 6 4. Wei Kang, T.; Mohd Taib, S.H.; Moozarm Nia, P.; Miyake, M.; Shameli, K. Synthesis and characterization
7 of Sn/Ag nanoparticle composite as electro-catalyst for fuel cell. J. Res. Nanosci. Nanotechnol. 2021, 1,
8 12–21.
- 9 5. Radziuk, D.; Shchukin, D.; Möhwald, H. Sonochemical design of engineered gold - Silver nanoparticles.
10 J. Phys. Chem. C. 2008, 112, 2462–8.
- 11 6. Khaydarov, R.A.; Khaydarov, R.R.; Gapurova, O.; Estrin, Y.; Scheper, T. Electrochemical method for the
12 synthesis of silver nanoparticles. J. Nanoparticle Res. 2009, 11, 1193–200.
- 13 7. Cataldo, F.; Ursini, O.; Angelini, G. Synthesis of silver nanoparticles by radiolysis, photolysis and
14 chemical reduction of AgNO₃ in *Hibiscus sabdariffa* infusion (karkadé). J. Radioanal. Nucl. Chem. 2016,
15 307, 447–55.
- 16 8. Mohd-Esa, N.; Hern, F.S.; Ismail, A.; Yee, C.L. Antioxidant activity in different parts of roselle (*Hibiscus*
17 *sabdariffa* L.) extracts and potential exploitation of the seeds. Food Chem. 2010, 122, 1055–60.
- 18 9. Da-Costa-Rocha, I.; Bonnlaender, B.; Sievers, H.; Pischel, I.; Heinrich, M. *Hibiscus sabdariffa* L. - A
19 phytochemical and pharmacological review. Food Chem. 2014, 165, 424–43.
- 20 10. Chen, J.H.; Wang, C.J.; Wang, C.P.; Sheu J.Y.; Lin, C.L.; Lin, H.H. *Hibiscus sabdariffa* leaf polyphenolic
21 extract inhibits LDL oxidation and foam cell formation involving up-regulation of LXR α /ABCA1
22 pathway. Food Chem. 2013, 141, 397–406.
- 23 11. Wang, J.; Cao, X.; Jiang, H.; Qi, Y.; Chin, K.L.; Yue, Y. Antioxidant activity of leaf extracts from different
24 *Hibiscus sabdariffa* accessions and simultaneous determination five major antioxidant compounds by LC-
25 Q-TOF-MS. Molecules. 2014, 19, 21226–38.
- 26 12. Świsłocka R. Spectroscopic (FT-IR, FT-Raman, UV absorption, ¹H and ¹³C NMR) and theoretical (in
27 B3LYP/6-311++G** level) studies on alkali metal salts of caffeic acid. Spectrochim. Acta. - Part A Mol.
28 Biomol. Spectrosc. 2013, 100, 21–30.
- 29 13. Catauro, M.; Barrino, F.; Poggetto, G.D.; Crescente, G.; Piccolella, S. Pacifico, S. New SiO₂/Caffeic acid
30 hybrid materials: Synthesis, spectroscopic characterization, and bioactivity. Materials (Basel). 2020, 13,
31 1–12.
- 32 14. Sharaf, S.; Higazy, A.; Hebeish, A. Propolis induced antibacterial activity and other technical properties
33 of cotton textiles. Int. J. Biol. Macromol. 2013, 59, 408–16.
- 34 15. Ismail, E.H.; Khalil, M.M.H.; Al Seif, F.A.; El-Maghdoub, F. Biosynthesis of gold nanoparticles using
35 extract of grape (*Vitis vinifera*) leaves and seeds. Prog. Nanotechnol. Nanomater. 2014, 3, 1–12.
- 36