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Green synthesis of silver nanoparticles using *Carica Papaya* fruit extract under sunlight irradiation and their colorimetric detection of mercury ions

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Abstract. We have successfully synthesized silver nanoparticles (AgNPs) by using aqueous extract of papaya (*Carica papaya*) fruit as bioreductant under sunlight irradiation without additional capping agent. Characterizations were done using UV-Visible spectrophotometry and Fourier Transform Infrared Spectroscopy (FTIR). The synthesized AgNPs have yellowish-brown color with surface plasmon resonance peak at 410 nm. Good selectivity of the AgNPs towards hazardous heavy metal of mercury ions in aqueous solution has been developed as a green environmental sensor. The presence of Hg(II) ions in the mixture changed the yellowish-brown color of AgNPs to colorless due to oxidation of Ag(0) in AgNPs to Ag(I) ions. Effect of samples matrix such as alkali metal, alkaline earth metal and transition metal ions were evaluated.

1. Introduction

The developments of silver (AgNPs) and gold nanoparticles (AuNPs) in recent years are significantly increased. They have potential applications in various fields such as chemistry, physics, biology, materials science, and medicine. AgNPs and AuNPs are highly efficient at absorbing and scattering light, different with many dyes and pigments, it has a color that depends upon the shape and size (10 – 100 nm) of the particles [1–3]. Due to its small particles size ($\sim 10^{-9}$ m) those results are in its large surface area. AgNPs and AuNPs have some unique optical, electrical, and thermal properties. The interaction of the AgNPs and AuNPs with light occurs due to the conduction electrons on the metal surface undergo an oscillation when excited by the light at specific wavelengths, known as surface plasmon resonance (SPR), this results in unusually strong scattering and absorption properties [4, 5].

In order to fabricate AgNPs from its salt AgNO_3 , it usually referred to bottom up fabrication; the chemical reducing agents such as NaBH_4 are widely used. However, the chemical reductants are not environmentally friendly. Alternatively, biosynthesis of AgNPs using plants, marine organisms and micro-organisms that abundance in our environment is now established as an emerging area of nanoscience research. The green synthesized AgNPs have been widely used as an anti-bacteria and sensor for heavy metals detection in environment [6–8].

Mercury, which has density of 15.53 g cm^{-3} , is well-known as toxic heavy metals. Among its compounds, methylmercury $\text{Hg}(\text{CH}_3)_2$, is the most toxic one [9]. Due to its mobilities in living systems and abilities to cross cell membranes, it is often bio-accumulated in fish and other organisms [10]. So far, mercury analysis is performed using bulk instruments such as ICP and AAS, which are



expensive and required laborious pretreatments. Here, we report a low-cost, portable and green protocol to analyze mercury in aqueous sample by means of AgNPs colorimetric method with sunlight irradiation assistance.

2. Experimental methods

2.1. Materials

Silver nitrate and other chemicals were supplied by Merck Ltd (Darmstadt, Germany). Papaya fruit was obtained from a local market in Indonesia. Double-distilled deionized water was used throughout the experiments. All glassware were washed with detergent 5%, HCl 4M, and water before use. A more detail washing and sampling procedures was published elsewhere [11].

2.2. Instruments

UV–Visible absorption spectra of the synthesized AgNPs were monitored using a BioSpectrometer (Eppendorf, Germany) in 270 – 700 nm range. Fourier Transform Infrared (FTIR) measurements were obtained on a Prestige 21 (Shimadzu, Japan). A Canon 30D digital camera (Tokyo, Japan) was employed to record the pictures.

2.3. Biosynthesis of silver nanoparticles

Fresh papaya fruits were washed with water to remove the dust. The 25 gram of fine-cut fruits was boiled with 50 ml of water at 80°C for 15 minutes. The extract was separated from the remaining small solids by filtration through Whatman no. 1 filter paper.

Silver nitrate with concentration 1 mM was prepared in Erlenmeyer flasks and the appropriate volume of fruit extract was added to the mixture under sunlight irradiation for 15 minutes. In order to optimize the AgNPs biosynthesis condition, a variation of different concentration of fruit extracts added into AgNO₃ solution were also conducted. The volume ratios of fruit extract to AgNO₃ were 1:5, 1:1, and 2:1. An aliquot of the mixture was taken periodically to monitor the progress of AgNPs biosynthesis by using UV–vis spectrophotometer. UV–vis spectra were recorded at a resolution of 1 nm. The pH of the reaction was kept at 4.5.

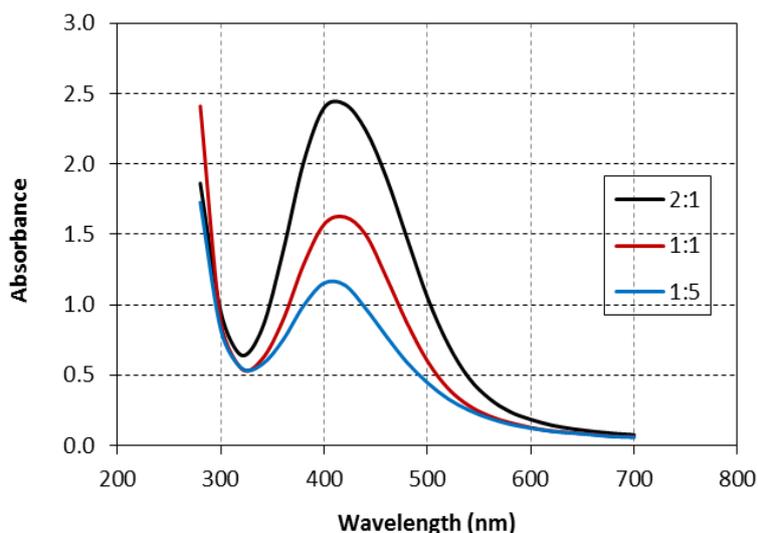


Figure 1. UV-Visible spectra of AgNPs fabricated by using papaya fruit extract at room temperature and with sunlight irradiation assistance. A peak absorbance of surface plasmon resonance was observed at 410 nm for all three different ratios of fruit extract to AgNO₃.

2.4. Colorimetric detection of mercury ions

An aliquot of freshly prepared AgNPs was put into transparent glass vials, then known concentration of Hg(II) and other metal ions (Al, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn) were added into the glass vials. Afterward, the absorption spectra were recorded using UV-visible spectrophotometer. The experiments of standards and samples were carried out under identical conditions to optimize the analytical performances. Simultaneously, the photographs were taken with a digital camera.

3. Results and discussion

Figure 1 shows UV-Visible spectra of AgNPs, which was fabricated using papaya fruit extract at room temperature with 15 minutes sunlight irradiation assistance. The best fruit extract to AgNO₃ solution ratio was 2:1. It is likely that lower concentration of fruit extract to AgNO₃ solution (1:5 and 1:1 ratios) was not sufficient to reduce Ag(I) quantitatively, thus more fruit extract exhibits better result as shown in figure 1. Colorless AgNO₃ was turned to yellowish-brown color of AgNPs colloid with an intense peak absorbance of surface plasmon resonance at 410 nm, which indicates a good dispersivity of 35 – 50 nm size of AgNPs in water [12]. Without sunlight irradiation, it took seven days (vs 15 minutes) to synthesize silver nanoparticles under the same conditions mentioned above.

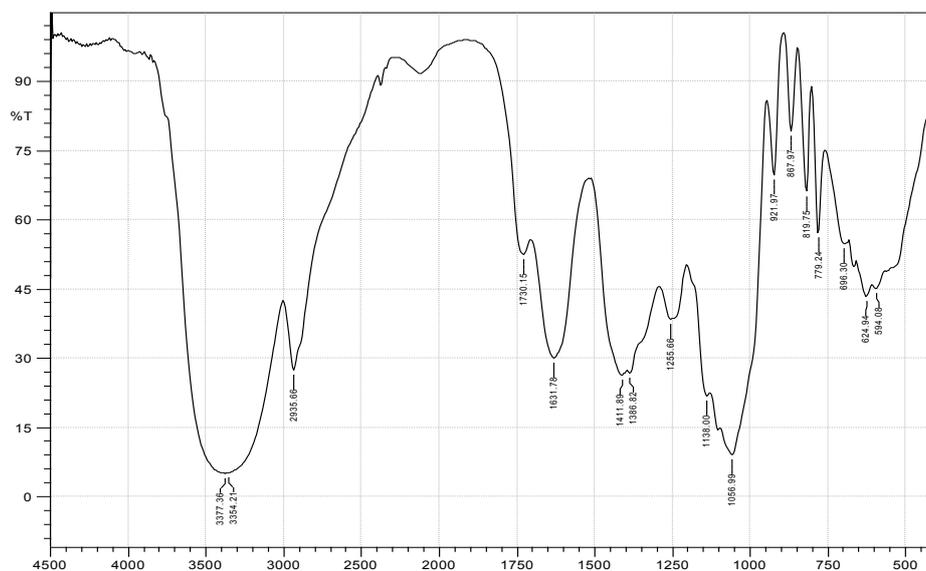


Figure 2. Fourier Transform Infrared (FTIR) spectra of dried powder of papaya fruit extract.

Table 1. Comparison of reagents for fabrication of NPs and its corresponding heavy metals detection.

Nanoparticles	Reagents	Detected heavy metals	References
AuNPs	NaBH ₄	Fe(III)	[16]
	Citrate	Cr(III), Cr(VI)	[17]
	Citrate	Hg(II), Ag(I)	[18]
	Citrate	Al(III)	[19]
	L-tyrosine	Hg(II), Pb(II), Mn(II)	[20]
AgNPs	NaBH ₄	Mn(II)	[21]
	Citrus extract	Hg(II)	[22]
	L-tyrosine	Hg(II), Pb(II), Mn(II)	[20]
	Soap-root plant	Hg(II)	[23]
	Papaya extract	Hg(II)	This study

High content of water-soluble organic compounds such as Vitamin C (ascorbic acid) and phenolic compounds in papaya fruit [13] may be attributed to its ability on reducing Ag(I) to Ag(0) in AgNPs green synthesis. Figure 2 shows FTIR spectra of papaya fruit extract that resemble those of ascorbic acid spectra [14]. Intense absorption bands at 3377 cm^{-1} can be assigned to O–H stretching of alcohols and/or phenols [15]. Absorption bands at 2935 cm^{-1} are characteristic of C–H stretching vibration. Medium bands at 1631 and 1056 cm^{-1} may result from the C=C ring stretching and C–OH bending vibration, respectively.

Table 1 shows the comparison of reagents that were previously used to synthesize nanoparticles and its corresponding heavy metals detection ability. Colorimetric method using AgNPs and AuNPs was used to analyze the concentration of various heavy metals such as Fe, Cr, Hg and Pb in aqueous environments at ppb level. The color changes of AgNPs and AuNPs were proportional to the heavy metals concentrations in sample, thus it is useful for qualitative and quantitative analysis.

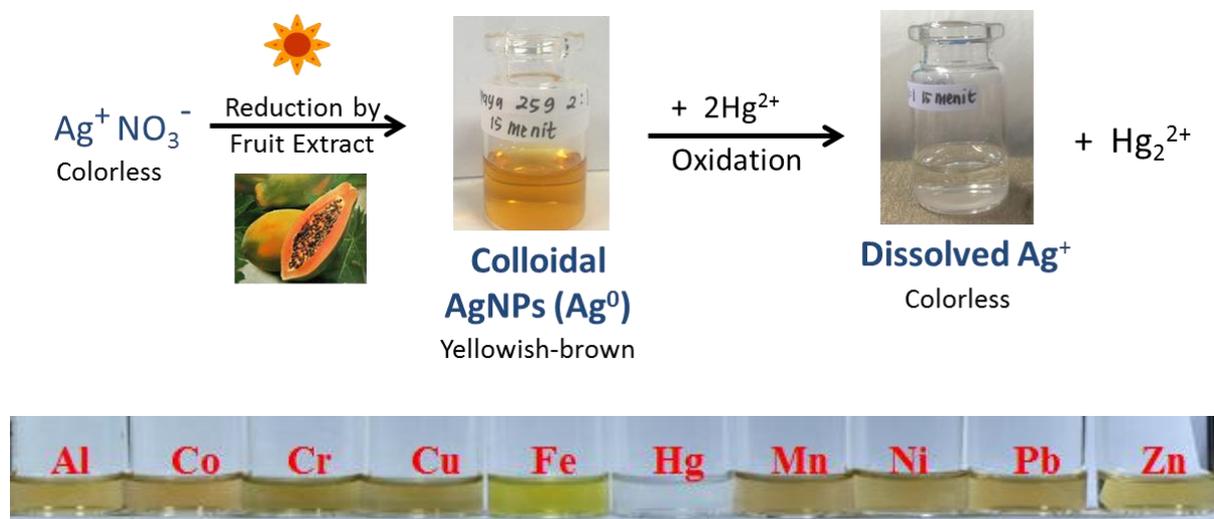


Figure 3. A schematic illustration of AgNPs formation using papaya fruit extract and Hg(II) colorimetric detection through redox reaction (upper scheme) and photograph of AgNPs selectivity test to various heavy metals (lower scheme).

A schematic mechanism of AgNPs formation using papaya fruit extract and Hg(II) colorimetric detection is shown in figure 3. Colorless AgNO_3 solution was turned to yellowish-brown color of AgNPs, and in the presence of Hg(II) ions, it turned back to colorless. The colorimetric detection was selective to only mercury ions. Other heavy metals, alkali and alkaline earth metals did not change the color of AgNPs. It is likely that reduction-oxidation reaction is the principle mechanism in AgNPs synthesis and mercury detection. As shown in table 2, the reduction potentials of Ag^+ and Hg_2^{2+} produced positive cell-potential (E_{cell}) while other metals produce negative cell-potential. The redox reaction with positive cell-potential resultant will be favoured, as shown in equations (1) to (4).

$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{red}} - E^{\circ}_{\text{ox}} \quad (1)$$



Table 2. Standard reduction potentials at 298°K. [24]

Reduction reaction	E ⁰ / V
Au ⁺ + e ⁻ → Au	+1.69
Au ³⁺ + 3e ⁻ → Au	+1.40
2Hg ²⁺ + 2e ⁻ → Hg ₂ ²⁺	+0,92
Hg ₂ ²⁺ + 2e ⁻ → Hg	+0,86
Ag⁺ + e⁻ → Ag	+0,80
Hg ₂ ²⁺ + 2e ⁻ → 2Hg	+0.79
Fe ³⁺ + e ⁻ → Fe ²⁺	+0,77
Cu ²⁺ + e ⁻ → Cu+	+0,16
Cr ³⁺ + 3e ⁻ → Cr	-0.74
Na ⁺ + e ⁻ → Na	-2,71

4. Conclusion

In this paper, we report the first attempt to fabricate AgNPs using papaya fruit extract as bioreductant with sunlight irradiation assistance, which can be completed within 15 minutes. Water-soluble bioactive compounds from papaya fruit extract that act as bioreductants of Ag(I) to form AgNPs were most likely ascorbic acid and other phenolic compounds. The as-prepared AgNPs have yellowish-brown color with surface plasmon resonance peak at 410 nm. The presence of Hg(II) ions in the mixture changed the yellowish-brown color of AgNPs to colorless due to oxidation of Ag(0) in AgNPs to Ag(I) ions. The detection procedure of the developed method could be a promising tool as a low-cost and portable method for real-time qualitative and quantitative mercury analysis in environments.

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References

- [1] Vahabi K and Dorcheh S K 2014 *Biosynthesis of Silver Nano-Particles by Trichoderma and Its Medical Applications, in Biotechnology and Biology of Trichoderma* (Amsterdam: Netherlands/ Elsevier) pp 393–404
- [2] Radhakumary C and Sreenivasan K 2011 *Analyst* **136** 2959–62
- [3] Chansuvarn W Tuntulani T and Imyim A 2015 *TrAC, Trends Anal. Chem.* **65** 83–96
- [4] Alarcon E I 2015 *Silver Nanoparticle Applications*, ed Emilio Alarcon May Griffith Klas I. Udekwu (Switzerland: Springer International Publishing) p 146
- [5] Gao Y X, Xin J W, Shen Z Y, Pan W, Li X and Wu A G 2013 *Sens. Actuators, B* **181** 288–93
- [6] Jain D, Daima K H, Kachhwaha S and Kothari S L 2009 *Digest J. Nanomater. Biostructures* **4** 557–63
- [7] Saxena A, Tripathi R and Singh R 2010 *Digest J. Nanomater. Biostructures* **5** 427–32
- [8] Ramesh P S, Kokila T and Geetha D 2015 *Spectrochim. Acta. A. Mol. Biomol. Spectrosc.* **142** 339–43
- [9] Nierenberg D W, Nordgren R E, Chang M B, Siegler R W, Blayney M B, Hochberg F, Toribara T Y, Cernichiari E and Clarkson T 1998 *The New Engl. J. Med.* **338** 1672–6
- [10] Clarkson T W, Magos L and Myers G J 2003 *The New Engl. J. Med.* **349** 1731–7
- [11] Firdaus M L, Darti P, Alwi W, Swistoro E, Sundaryono A and Ruyani A 2015 *AIP Conf. Proc.* vol 1677 (New York: Melville/ AIP Publishing) p 110003
- [12] Perez D P 2010 *Silver Nanoparticles*, ed Perez D P (Croatia: In-Tech)
- [13] Gayosso-García Sancho L E, Yahia E M and González-Aguilar G A 2011 *Food Res. Int.* **44** 1284–91

- [14] Panicker C Y, Varghese H T and Philip D 2006 *Spectrochim. Acta, Part A* **65** 802–4
- [15] Schulz H and Baranska M 2007 *Vib. Spectrosc.* **43** 13–25
- [16] Wu S P, Chen Y P and Sung Y M 2011 *Analyst* **136** 1887–91
- [17] Chen W, Cao F, Zheng W, Tian Y, Xianyu Y, Xu P, Zhang W, Wang Z, Deng K and Jiang X 2015 *Nanoscale* **7** 2042–49
- [18] Lou T, Chen Z, Wang Y and Chen L 2011 *ACS Appl. Mater. Interfaces* **3** 1568–73
- [19] Chen S, Fang Y M, Xiao Q, Li J, Li S B, Chen H J, Sun J J and Yang H H 2012 *Analyst* **137** 2021–3
- [20] Annadhasan M, Muthukumarasamyvel T, Sankar B V R and Rajendiran N 2014 *ACS Sustain. Chem. Eng.* **2** 887–96
- [21] Zhou Y, Zhao H, Li C, He P, Peng W, Yuan L, Zeng L and He Y 2012 *Talanta* **97** 331–5
- [22] Ravi S S, Christena L R, SaiSubramanian N and Anthony S P 2013 *Analyst* **138** 4370–7
- [23] Farhadi K, Forough M, Molaei R, Hajizadeh S, and Rafipour A 2012 *Sens. Actuators, B* **161** 880–5
- [24] Atkins P and Paula J de 2009 *Physical Chemistry* (UK: Oxford/ W H Freeman)