



Green Chemistry Formation of Stable Ag Nanoparticles (AgNPs) In Isopropanol Solvent

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ABSTRACT

Several bioreduction processes become appreciation for the synthesis of silver nanoparticles (AgNPs) because of their multiple applications, cost effective and eco-friendly. The main problems in the synthesis of AgNPs are colloidal systems agglomeration and damage due to precipitation. In this study, it has been investigated the use of *Uncaria Gambir Roxb* leaf extract as bioreductor and capping agent on the synthesis of AgNPs and isopropanol as a solvent. XRD studies showed that the AgNPs are crystalline fcc (face center cubic) without another phase and AgNPs size in isopropanol solution was smaller than aqueous solution. TEM images indicated that the obtained AgNPs are predominantly spherical shape, with sizes in the range of 10 to 30 nm.

Keywords: Silver nanoparticles, bioreductor, isopropanol solvent, *Uncaria Gambir Roxb*.

INTRODUCTION

In recent years, research on the synthesis of metal nanoparticles has been widely discussed and has become a major topic due to their new or improved chemical, optical, electric, and magnetic properties compared to their bulks ¹. Among them,

silver nanoparticles (AgNPs) have been a focus of many researchers not only because of their properties but also because silver nanoparticles have been widely used as an antimicrobial property². Their properties strongly depend on their size and shape, and therefore it is very important to be able to finely control the morphology of the nanoparticles.

Several methods have been used in the formation of AgNPs such as the reduction in solution, electroless, photochemical reduction, hydrothermal, and assisted-microwave synthesis. So far, several weaknesses have been found, including the need for sophisticated and more expensive equipment. They also have high toxicity properties and more particularly difficult to obtain a stable colloid.

A green synthesis method is an attractive option at this time where the synthesis of AgNPs uses various extracts of the leaves of plants including the most leaves that have flavonoid compounds in the presence of polyphenols structure such as *Rumex hymenasepalus*³, *Artocarpus heterophyllus*⁴, *Camellia Sinensis*⁵, *Mollugo nudicaulis*⁶ and *Azadirachta indica*⁷ which can reduce Ag(I) to Ag(0). Ramachandran *et al*⁸ and Siavash Iravani⁹ have reviewed various kinds of plant extracts that have been used in the synthesis of metal nanoparticles, especially Ag nanoparticles. In general, the resulting nanoparticles of this process have size in the range of nanosize with spherical and triangular structures¹⁰⁻¹².

In the case of metal oxides, solvent is a factor that determines the stability and also controls the size and shape of the particles¹³. In our previous studies, it has been reported that the use of leaf extracts bioreducing gambier was able to act as reducing agent in the formation of silver nanoparticles in aqueous solvent. AgNPs with sizes of 25 - 40 nm have been obtained with the help of a hydrothermal process¹⁴. In this study we report biosynthesis of AgNPs by reduction of silver nitrate (AgNO_3) in isopropanol solution using isopropanol - Gambier leaf extract in order to control the shape and size of silver nanoparticles.

MATERIALS AND METHODS

Plant material and preparation of extracts

All chemicals used for this reaction were of analytical grade and obtained from Merck without any further purifications. Gambier leaves were collected from agricultural field located at Payakumbuh – West Sumatera, Indonesia. Fresh leafs of Gambier were washed thoroughly with double distilled water. Dried leaf were incised and crushed into small pieces. Approximately 5 g of those finely Gambier

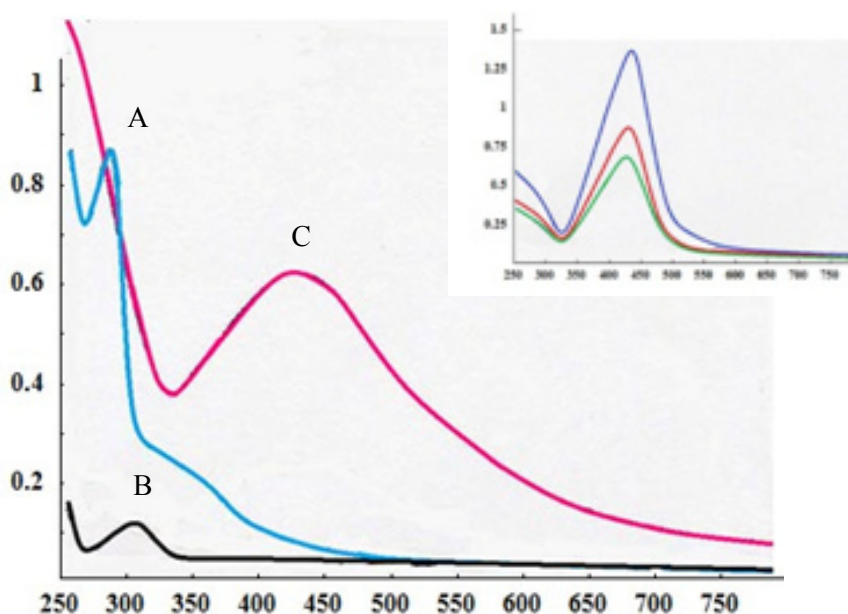


Fig. 1: The absorption of the plant extract (A), pure AgNO_3 solution (B), and a sample of AgNPs with reaction time of 4 h (C)

were weighted and transferred into a 200 ml beaker containing 50 ml isopropanol, mixed well and boiled for 30 minutes. The extract obtained was filtered

through filter paper and the filtrate was diluted and collected to 250 ml with isopropanol. The solution was kept in refrigerator for further use.

Synthesis of AgNPs

The Ag Nanoparticles from Gambier leaves extract was prepared as previously described method with slightly modifications¹⁴. Isopropanol solution (5 mM) of silver nitrate (AgNO_3) was prepared and used for the synthesis of silver nanoparticles. An amount of 10 ml of extract was added to 40 ml of 5 mM AgNO_3 solution. After addition of extracts, the color of the AgNO_3 solution altered to brown. The effect of reaction times on the synthesis of silver nanoparticles was carried out and evaluated every 10 minutes. The precipitate was separated by high speed centrifugation at 6000 rpm. The separated solid mass was washed three times with ethanol to remove the organic alcohol soluble impurities. Product was dried in oven at 50C for 2–3 h. Finally, it was transferred into light resistant containers for further characterization.

Characterization

UV–vis spectroscopic studies were carried out on a Thermo spectrophotometer. The sample for XRD measurement was prepared by depositing a dried sample on a slide and the diffraction pattern was recorded on a PANalytic X'PERT-PRO X-ray spectrometer. The size of the nanoparticles was calculated by the Scherer's equation. High resolution-transmission electron microscopic (HR-

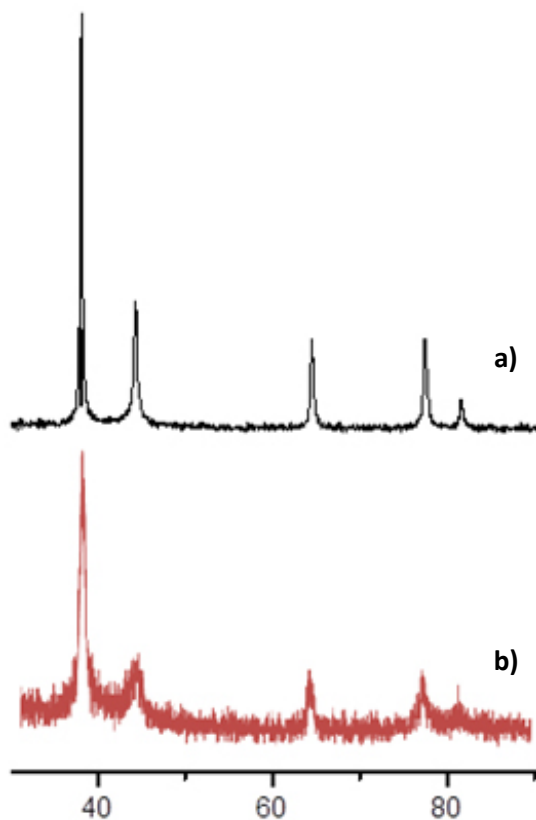


Fig. 2: XRD patterns of synthesized AgNPs using different solvent, a) in aqueous solution, b) Isopropanol solution

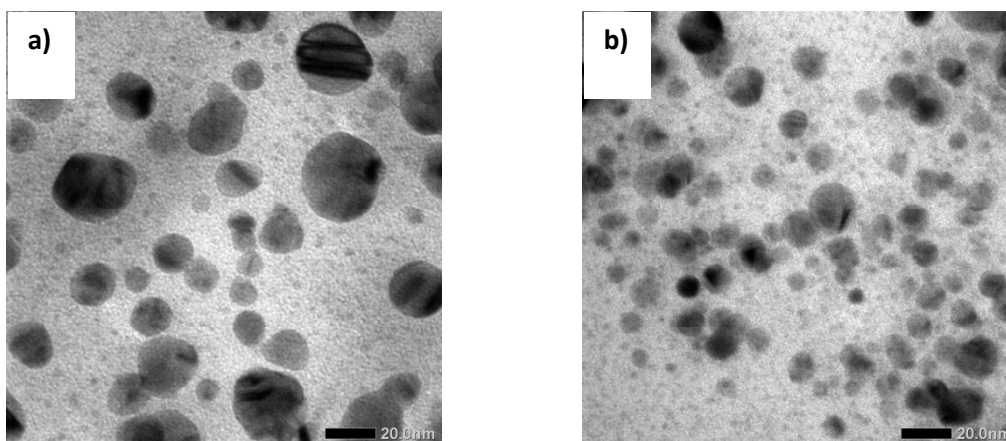


Fig. 3: TEM images of the AgNPs at different solvents, a) in aqueous solution, b) Isopropanol solution

TEM) measurements were done using a Shimadzu CTLA-4 microscope.

RESULTS AND DISCUSSIONS

UV-vis analysis

The addition of the extract into 5 mM of AgNO₃ solution changed color from pale yellow to brownish within 5 minutes. The color is more intense with increasing time of reaction. The change in color is due to the strong absorption of visible light due to excitation of the nanoparticle surface plasmons¹⁵. This is a strong indication of the formation of silver nanoparticles. In Figure 1, the curves demonstrate the absorption of the the plant extract (A), pure AgNO₃ solution (B), and a sample of AgNPs with reaction time for 4 h (C). The polyphenol peak (observed in the Gambir extract) is also clearly visible around 278 nm, while the UV-Vis spectra of the AgNO₃ solution has a peak around 305 nm, as expected for Ag⁺ ions. These spectral studies identify the formation of stable nanoparticles of silver (insert: highest peak for one week). The maximum absorption shows the appearance of a single and strong surface plasmon resonance band absorption peak centered at about 427 nm, which indicates that these particles are isotropic in shape and relatively uniform in size.

X-Ray diffraction (XRD)

The XRD analysis is performed to confirm the crystalline nature of AgNPs that prepared by using Gambier extract as bioreductor. Various Bragg's reflections are clearly visible in silver XRD pattern, which are corresponding to the (111), (200), (220) and (311) set of lattice planes, and also agreed by joint committee of powder diffraction standard (JCPDS) Card No- 04-0783 (Fig. 2). On the other hand, the difference in solvent gives different peak sharpness and heights. Peaks obtained from aqueous solution are sharper and higher than isopropanol solution. Based on the equation Scherer, a sharp and height peak gives larger crystal size than the width and low peak. This will be proved later by TEM.

Transmission Electron Microscope (TEM)

The typical TEM images of AgNP-Gambier Isopropanol and aqueous solution are given in Fig. 3. The images show that the nanoparticles synthesized using Isopropanol as solvent are almost spherical and slightly polydispersed. The size of AgNPs is ca. 10–25 nm according to the TEM image, and that is consistent with the published data for the synthesis of AgNPs by the chemical reduction method¹⁶. The TEM images show good stabilization of silver nanoparticles due to interaction with the Gambier – isopropanol solution. Based on ionic strength, water media is more powerful than isopropanol media. Their electrophoretic mobility is freer in aqueous media due to faster growth of nanoparticles. Organic media (isopropanol solvent) is absorbed on to these nanoparticles significantly reducing the aggregation and improving its AgNPs stability.

CONCLUSION

We have demonstrated a green chemistry approach for the synthesis of silver nanoparticles at ambient reaction conditions using *Uncaria Gambier Roxb* leaf extract and isopropanol solvent. The leaf extract acts as reducing agent as well as stabilizing/capping agent. These biosynthesized AgNPs are highly stable for several weeks in isopropanol solution. XRD studies show that the AgNPs are crystalline fcc (face center cubic) and particles size is of 20 nm using isopropanol solution. TEM images indicate that the obtained AgNPs are predominantly spherical shape, with sizes in the range of 10 to 30 nm.

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