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# A green synthesis method for large area silver thin film containing nanoparticles

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ABSTRACT

The green synthesis method is inexpensive and convenient for large area deposition of thin films. For the first time, a green synthesis method for large area silver thin film containing nanoparticles is reported. Silver nanostructured films are deposited using silver nitrate solution and guava leaves extract. The study confirmed that the reaction time plays a key role in the growth and shape/size control of silver nanoparticles. The properties of silver films are studied using UV–visible spectrophotometer, scanning electron microscopy (SEM), X-ray diffraction (XRD), atomic force microscopy (AFM), contact angle, Fourier-transform Raman (FT-Raman) spectroscopy and Photoluminescence (PL) techniques. Finally, as an application, these films are used effectively in antibacterial activity study.



## 1. Introduction

Silver nanoparticles exhibit outstanding electrical, optical, magnetic, catalytic, etc. properties that cannot be exposed by their bulk state [1,2]. These outstanding properties of silver nanoparticles energetically depend on size and shape of nanoparticles, their interactions with stabilizers and surrounding media and also on the manner of their preparation. Therefore, the controllable synthesis of silver nanocrystals is a key challenge to achieve their better applied characteristics [3].

During synthesis of silver nanoparticles in bulk from, various chemical and physical method parameters are responsible for controlling the shape and size of silver nanoparticles. Such methods include as photoinduced [4,5], electrochemical [6], ultrasonic assistant [7], solvo thermal [8,10] and heat evaporation [11]. In silver synthesis process, passivator reagents like thiophenol, thiourea and marcapto acetate are needed to prevent nanoparticles from aggregation. These passivators are toxic if these nanoparticles are used in medical applications and are also responsible to pollute the environment if large scale nanoparticles are produced [12].

To overcome above problems, an alternative inexpensive, reliable, safe and ecofriendly green synthesis routes are used. Green synthesis routes can be used for large scale synthesis. Also, there is no need to use high pressure, energy, temperature and toxic chemicals [13]. These green synthesis routes include different methods like polyoxometallates, polysaccharide, tollens, irradiation and biological [14]. Out of these, biological method using extract of plant leaves has shown a great potential in the synthesis of silver nanoparticles in comparison with chemical and physical routes.

Recently, several groups are successful in the synthesis of silver nanoparticles using leaves extracts obtained from plants as a reducing agent, e.g. neem [15], anacardium occidentale [16], curry [17], hibiscus [18], lemon [19], guava [20], etc. Out of these, extract of guava leaves is a potential reducing candidate for the synthesis of silver nanoparticles. The presence of high quantity terpenoids, flavonoids, polysaccharides, proteins and alkaloids in guava leaves extract are responsible for formation of silver nanoparticles. On the other hand, other parts of the guava tree including the fruit, stem and root extracts are not useful for reduction of silver ions ($Ag^+$) to silver ($Ag^0$) nanoparticles, because of the presence of chloride content the solution results into white precipitation. Therefore, leaf is the only part of guava tree used in the reduction to silver ($Ag^0$) nanoparticles [20].

For large area application, there is a necessity to design a method to synthesis silver nanoparticles in the form of thin film over a substrate supported it. Thin film is any solid or liquid system that possesses two dimensional order of periodicity. Large area thin films can be fabricated using physical and chemical methods. Among these, chemical methods are easy to synthesis, inexpensive and low cost. Pawar et al. discussed the chemical synthesis of metal oxide and chalcogenide thin films and their applications for supercapacitor, solar cell and gas sensor [21].

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Few groups have already synthesized silver thin films using chemical reduction method adopting various solvents and reducing agents. For e.g., deposition of silver thin film was carried out using formaldehyde solution [22,23]. Lee et al. synthesized silver thin films by spin coating method in which gel was prepared using isopropyl alcohol [24]. Also the silver nanoparticles are loaded on the surface of the titanium thin film by dip coating method using methanol as a solvent [25]. Khan et al. synthesized silver thin films by dip coating method. To avoid silver nanoparticles from agglomeration, many chemicals such as glucose, polyvinylpyrrolidone and sodium hydroxide have been used [26].

In the present work, green synthesis chemical route is used for deposition of large area silver nanoparticles containing film. The silver films with different thicknesses are deposited on large area glass substrates. The effect of film thickness on structural, morphological, optical properties, etc. is investigated. Finally its antibacterial activity is tested.

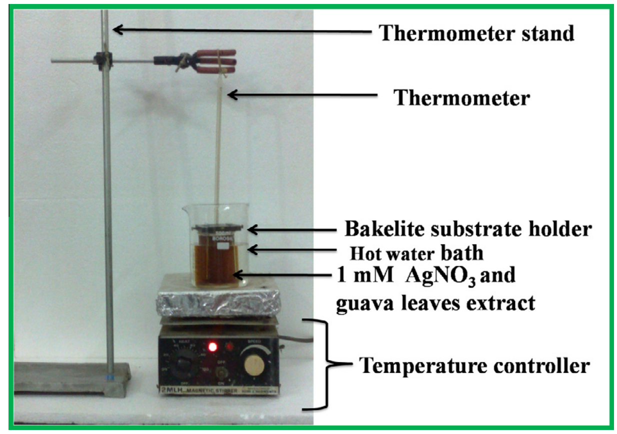


**Fig. 2.** Photograph of experimental setup of chemical deposition method.

## 2. Experimental details

### 2.1. Materials

The photograph of fresh leaves collected from guava tree from garden of Department of Physics, Shivaji University Kolhapur is shown in Fig. 1. For the preparation of leaves extract, fresh leaves were thoroughly rinsed with deionized water. After carefully removing midribs of guava leaves, 5 gm guava leaves were chopped into small pieces. The chopped leaves were boiled in 100 ml of deionized water for 10 min. The leaves extract was then cooled and filtered through filter paper (Whitman No. 1). The color and translucency of the leaves extract containing bottle is shown in inset of Fig. 1. Silver nitrate ($AgNO_3$) procured from S.D. Fine Chemical Ltd., India is used as a silver ion source.

### 2.2. Preparation of silver thin films

Fig. 2 shows the experimental setup for the deposition of silver thin films on to glass substrate. The $AgNO_3$ solution and guava leaves extract were used as the source of $Ag^+$ ions and reducing agent, respectively. The chemical bath was formed by mixing equal volumes of 1 mM silver nitrate ($AgNO_3$) solution and 5 gm guava leaves extract. The pH of the resulting solution was 3 ± 0.1. Previously cleaned glass substrates were immersed in the chemical bath and then the bath was heated at 313 K for different time intervals (10–30 min). After about 30 min, the solution became dark brown and precipitate was formed in the bath. During the precipitation, the heterogeneous reaction occurred and the deposition of silver thin films containing nanoparticles took place on the glass substrates. The substrates coated with dark brown colored film were removed, rinsed and dried in air. The silver films obtained with above concentration were uniform and well adherent to the glass substrate. The higher concentration of precursor solutions resulted into a higher growth rate but the quality of the film was poor due to the powdery deposit.

**Fig. 1.** Photograph of guava leaves (inset shows bottle containing guava leaves extract).

In order to demonstrate the feasibility of chemical deposition method, different thicknesses with large area (>20 $cm^2$) silver thin films were deposited.

### 2.3. Characterization techniques

The crystal structure of the silver thin films was identified by X-ray diffraction analysis using D2 PHASER model purchased from bruker AXS Analytical Instruments Pvt with Cu ($\lambda$ = 1.5404 Å) target. The surface morphology was visualized using a Model JEOL-6360 scanning electron microscope. The Raman spectrum of the films was recorded in the spectral range of 500–1500 $cm^{-1}$ using Raman spectrometer (Bruker MultiRAM, Germany Make). The optical absorption study was carried out within a wavelength range of 350–850 nm using a UV-1800 SHIMADZU spectrophotometer, with glass substrate as a reference. The wettability of the film was studied with contact angle meter purchased from Ramehart (USA equipment with CCD camera). The room temperature photoluminescence was investigated using Perkin Elmer LS-55 using Xenon excitation source. The topographic images of the assemblies on the glass were recorded with a multimode atomic force microscope (Innova-1B3BE) operated in the contact mode. The thickness of film was computed using fully computerized AMBIOS Make XP-1 surface profiler.

## 3. Results and discussion

### 3.1. Film formation mechanism

Biosynthesized nanoparticle containing silver thin films are obtained using chemical method, wherein thin film formation is based on the formation of solid phase from a solution.

In colloidal containing silver nanoparticles, formation of a bulk state silver nanoparticle occurs upon the transformation of a supersaturated solution to the saturated state. Two distinct steps, nucleation and subsequent particle growth, are involved in this process. During nucleation, clusters of silver metal precursor