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Letter

# Black pepper assisted biomimetic synthesis of silver nanoparticles

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ABSTRACT

In this paper, we report biomimetic synthesis of silver nanoparticles using crude black pepper (*Piper nigrum*) extract at room temperature. X-ray diffraction (XRD) pattern suggests the formation and crystallinity of silver nanoparticles. The average particle size of silver nanoparticles was found in the range of 20–50 nm as confirmed by Transmission electron microscopy (TEM). UV–vis absorption shows a characteristic absorption peak of silver nanoparticles at 410 nm. This synthesis approach is cost effective, eco-friendly and promising for the biosensing and nanoelectronic applications.



## 1. Introduction

The synthesis and characterization of noble metal nanoparticles are an important area of research related to the size and shape of nanoparticles, which provides not only an efficient control over physicochemical properties but also their potential applications in the various sectors including catalysis, sensor technology, biological labeling, optoelectronics recording media and optics [1–8]. The size, shape and surface morphology play crucial roles in controlling the physical, chemical, optical and electronic properties of the nanoscopic materials [9,10]. Various methods are available for nanoparticles synthesis based on the physicochemical methods, but the most of these methods are highly reactive and causes potential environmental and biological hazards [11]. Biomimetics have advantages over physicochemical methods because of its clean, non-toxic chemicals, environmentally benign solvents, and user-friendly nature [12]. Shankar et al. reported the synthesis of gold and silver nanoparticles by the reduction of aqueous $AuCl_4^-$ and $Ag^+$ ions using extracts from geranium, neem and lemongrass plants and they revealed that the gold nanotriangles showed that ketones/aldehydes present in the extract may play an important role in directing the shape evolution in these nanostructures. Ankamwar et al. reported the synthesis of gold nanotriangles using tamarind leaf extract as the reducing agent and identified that tamarind plant as a potential candidate for shape-controlled synthesis of gold nanoparticles due to tartaric acid (–COOH) [13–17].

In this present study, we report on the synthesis of silver NPs using black pepper seed extract at room temperature. This synthesis approach is simple, cost effective, stable for long time, reproducible, eco-friendly and promising for the biosensing and nanoelectronic applications.

## 2. Experimental

The chemicals and reagents were used with high quality and purity (Merck, Germany). The sample was characterized by X-ray diffraction (Rigaku, model D/max 2200 H/PC XRD, Japan) using CuKα radiation (0.154 nm) at a scanning rate of 5°/min, TEM (FEI, model Tecnai $G^2$, Netherland), at an accelerating voltage of 300 kV and UV–vis absorption spectrum (Perkin Elmer model L35, Germany). The particle size was calculated via Image J software (Image processing and analysis in JAVA, France).

Weighed 10 g black pepper seeds and washed thoroughly with distilled water and air-dried. After that powdered the seeds and boiled in 50 ml distilled water for 10 min. The cooled filtrate was adjusted at pH 12 by adding 1 M NaOH. Took 100 ml of 10 min $AgNO_3$ in a conical flask and added 1.0 ml of extract drop by drop. Put the above solution on magnetic stirrer for 2 h and centrifuged at 3000 rpm for 10 min, supernatant decanted off and residue collected. Residue was washed three times with double distilled water followed by ethanol. Finally, residue kept in vacuum oven at 80 °C for 10 h. The residue was used for the characterization by various techniques. The proposed synthesis was illustrated in Fig. 1.

## 3. Results and discussion

Black pepper broth is known to contain several biomolecules such as alkaloids, proteins, polysaccharides, amino acids and vitamins. These biomolecules could be used as bioreductants to react with metal ions and they could also be used as scaffolds/template to direct the formation of nanoparticles in solution. The mechanism responsible for the reduction may postulate as follow: the silver ions were trapped on the surface of proteins/or predominated alkaloid piperine in the extract via electrostatic interactions. This stage

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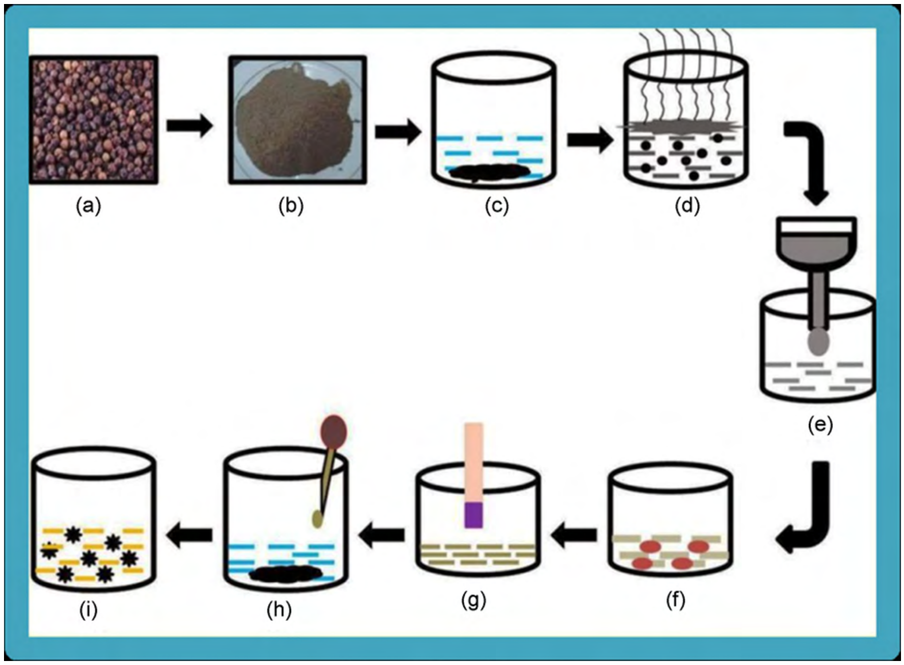


**Fig. 1.** Shows schematic representation of silver nanoparticles synthesis: (a) black pepper buds, (b) washed, dried and crushed black pepper, (c) black pepper in 50 ml distilled water, (d) boiling of aqueous solution of black pepper for 10 min, (e) filtration of extract, (f) pH maintaining to 12 with NaOH, (g) pH testing of black pepper extract, (h) mixing of extract in $AgNO_3$ solution, and (i) formation of silver nanoparticles.

was the recognition process. The silver ions were then reduced by the proteins leading to changes in their secondary structure and the formation of silver nuclei. The silver nuclei subsequently grew by the further reduction of silver ions and their accumulation of the nuclei.

Fig. 2 shows XRD pattern of the dried sample using CuKα radiation (0.154 nm) at a scanning rate of 5°/min for 2$\theta$ ranging from 20° to 80°. The XRD pattern confirms the face-centered-cubic (fcc) lattice (JCPDS file no. 04-0783) with strong diffraction peaks at 37, 44, 66 and 77 degrees of 2$\theta$ which corresponds to (1 1 1), (2 0 0), (2 2 0) and (3 1 1) crystal planes. There was no significant change in the peak position of silver nanoparticles formation before and after heating the sample as depicted in Fig. 2. No broad amorphous peak in between 20° and 35° of 2$\theta$ was appeared before and after heating of the sample, suggesting that the black pepper extract acts as a reducing agent not as a template (substrate). Even though, in the heated sample, no other diffraction peaks could be detected, i.e., phase-pure metal silver formation. In the XRD pattern, one sharp and strong diffraction peak centered at 37° was appeared, which can be indexed to the (1 1 1) reflection of the metallic silver with fcc structure (JCPDS File No. 04-0783). The weak diffraction peaks at 44°, 66° and 77° in the pattern agrees well with the (2 0 0), (2 2 0) and (3 1 1) reflections. Thus, the XRD pattern suggesting that the product is purely silver nanoparticle with high crystallinity.

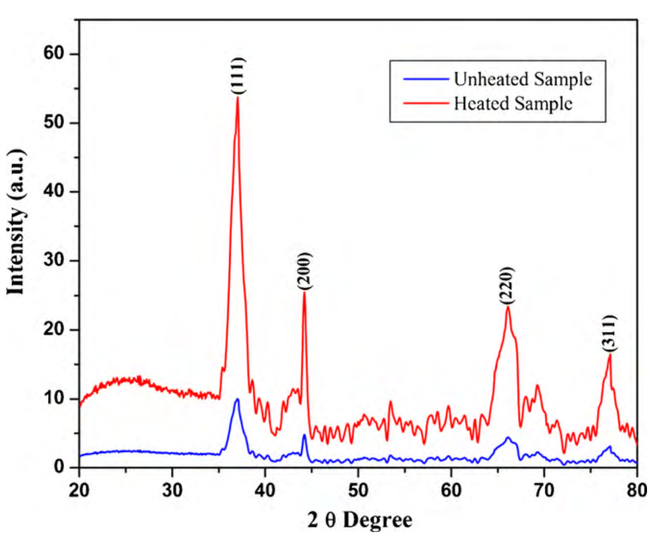


**Fig. 2.** Shows XRD pattern of silver nanoparticles synthesized by biomimetic method using black pepper showing strong diffraction peaks of silver at 37°, 44°, 66° and 77° of 2θ which corresponds to (1 1 1), (2 0 0), (2 2 0) and (3 1 1) crystal planes in heat treated and untreated sample.

Fig. 3 shows TEM image of the sample, reveals spherical shape with an average particle size between 20 and 50 nm. Selective area electron diffraction (SAED) pattern exhibits a set of rings containing spots (Fig. 3, inset) suggesting that nanoparticles have a larger grain size, uniform shape and polycrystalline in nature. Fig. 4 shows a particle distribution of almost spherical shapes and with sizes in the range among 20 and 50 nm.

Fig. 5 shows UV–vis absorption spectrum of the sample, recorded in the wavelength range of 250–550 nm. The shape of the plasmon band is almost symmetrical, suggesting that the nanoparticles are well-dispersed and uniform in shape. If nanoparticles are not uniform, then it leads to a broad absorption peak at higher wavelength and splitting of a plasmon band into two bands [18]. Silver nanoparticles are known to exhibit a size-dependent characteristic surface plasmon resonance band that can be measured using UV–vis spectroscopy. We observed a characteristic surface plasmon absorption band at 410 nm in our silver nitrate solution incubated with the black pepper broth at 2 h. The plasmon bands are broad with an absorption tail in the longer wavelengths. This broadening of the plasmon band could be in principle due to the size and shape distribution of the particles. As expected, black pepper exhibited silver precipitation, and the UV–vis spectrum of the solution showed distinct absorption, i.e., 302 nm (blue shift) as shown in Fig. 5. The main biochemical difference between the silver precipitating black pepper and alone is the overall charge of

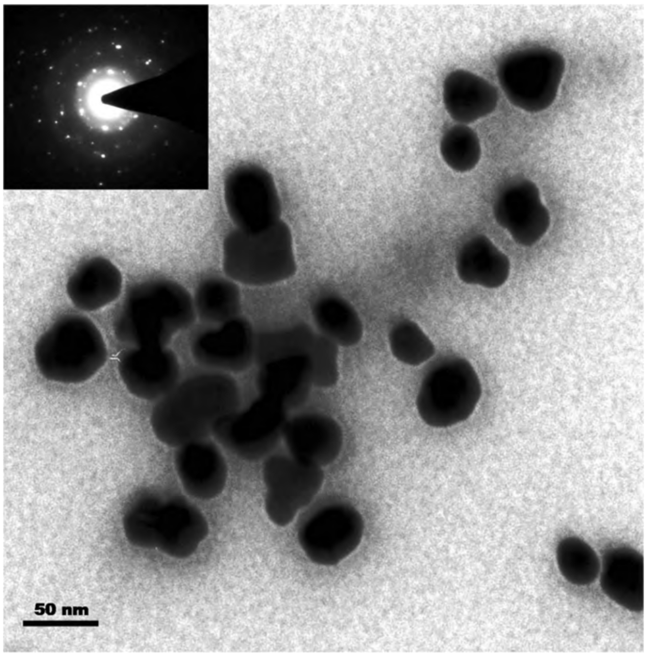


**Fig. 3.** Shows TEM image suggesting silver nanoparticles size. Inset shows SAED pattern.

the biomolecules. Based on these assumptions, the silver-surfacing biomolecules including predominant alkaloids (especially piperine and piperidine) are responsible for precipitating silver from an aqueous reaction solution medium of silver ions. Several basic amino acids as well as other non-silver surfacing bioconstituents may also be responsible for the precipitating silver from the same.

UV–vis spectra in Fig. 5 revealed as: (A) spectrum shows peak at 410 nm while completion of reaction in reaction mixture after 2 h. After termination of reaction or collected powder solution shows peak at 302 nm, i.e., blue shift of peak, suggesting desired Ag NPs formation via black pepper assisted approach (B). Spectrum (C) shows the black pepper broth with NaOH treated (maintained at pH 12), suggesting many peaks at UV wavelengths suggesting the basic amino acids or alkaloids, they might play role for AgNPs formation. Whereas, spectrum (D) shows the black pepper broth without NaOH treated, no peak appeared. However, work is in progress for deciphering the exact biomolecules of black pepper for playing crucial role to establish systematic AgNPs formation mechanism.

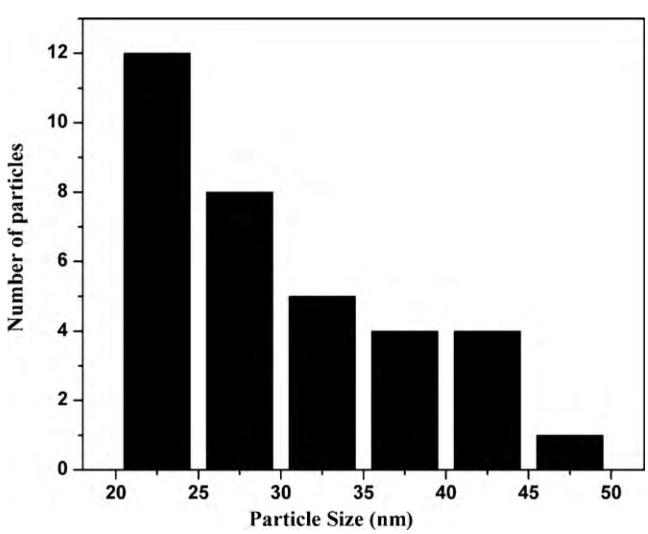


**Fig. 4.** Shows particle size distribution histogram.

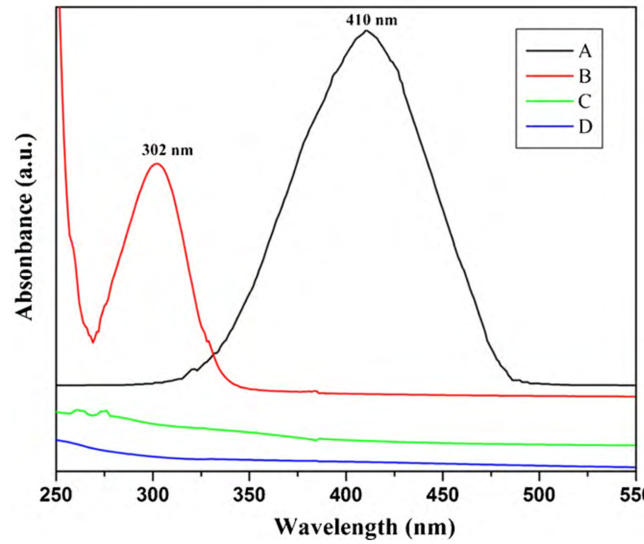


**Fig. 5.** Shows UV–vis absorption spectra of silver nanoparticles formation. (A) AgNPs formation during reaction at 2 h, (B) AgNPs after termination of reaction, i.e., powdered sample, (C) NaOH treated black pepper extract (pH 12) and (D) black pepper extract without NaOH.

## 4. Conclusions

In this manuscript, we have established for the first time a novel biomimetic synthesis of silver nanoparticle using black pepper extract at room temperature. The black pepper extract was boiled and filtered and maintained its pH at 12 by adding NaOH solution. The optimal volume of extract added into the optimal concentration of $AgNO_3$ solution for 2 h incubation time onto the magnetic stirrer setup. The formation of silver nanoparticle by biomimetic route opens the new avenues over chemical routes because of its cost effective and eco-friendly nature. XRD, TEM and UV–vis techniques were used to confirm the silver nanoparticles formation. The alkaloid piperine (or few basic amino acids or both) of the black pepper seed extract plays a leading role for the formation and stabilization of Ag NPs, respectively. Our findings could be targeted for the promising potential applications including water purification, recording media, biosensing devices, nanoelectronic, and catalysis.

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