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# Capuli cherry-mediated green synthesis of silver nanoparticles under white solar and blue LED light

Brajesh Kumar*, Yolanda Angulo, Kumari Smita, Luis Cumbal, Alexis Debut

*Centro de Nanociencia y Nanotecnologia, Universidad de las Fuerzas Armadas-ESPE, Av. Gral. Rumiñahui s/n, Sangolqui P.O. BOX 171-5-231B, Ecuador*

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ABSTRACT

In this article, the Capuli (*Prunus serotina* Ehrh. var. Capuli) cherry extract was used for the synthesis of silver nanoparticles (AgNPs) in the presence of white/visible solar and blue light-emitting diode (LED) light. For the characterization of the extract and the AgNPs, Fourier transform infrared spectroscopy and ultraviolet–visible spectroscopy were employed, along with hydrodynamic particle size analysis, transmission electron microscopy and X-ray diffraction. The Ag nanospheres obtained using white light were 40–100 nm in diameter and exhibited an absorption peak at $\lambda_{max}$ = 445 nm, whereas those obtained using blue LED light were 20–80 nm in diameter with an absorption peak at $\lambda_{max}$ = 425 nm. Thermal analysis revealed that the content of biomolecules surrounding the AgNPs was about 55–65%, and it was also found that blue LED light AgNPs (56.28%, 0.05 mM) had a higher antioxidant efficacy than the white solar light AgNPs (33.42%, 0.05 mM) against 1,1-diphenyl-2-picrylhydrazyl. The results indicate that obtaining AgNPs using a blue LED light may prove to be a simple, cost-effective and easily reproducible method for creating future nanopharmaceuticals.



## Introduction

There has been a continued and considerable interest in nanoparticles for the last few decades owing to the unique properties they display with decreasing size or structural units. Among inorganic-based nanomaterials, silver nanoparticles (AgNPs) are of special interest and are advantageous in the areas of biomolecular detection and diagnostics (Schultz, Smith, Mock, & Schultz, 2000), therapeutics (Eckhardt et al., 2013), catalysis (Kumar, Smita, Cumbal, Debut, & Pathak, 2014), micro-electronics (Gittins, Bethell, Nichols, & Schiffrin, 2000), and many other biomedical and engineering applications. Recently, green synthesis of AgNPs using plant materials has been gaining increased attention because of its ease of preparation, cost effectiveness, and lack of hazardous reagents (Akhtar, Panwar, & Yun, 2013). Plant materials, including leaves (Kumar, Smita, Cumbal, & Debut, 2014a), flowers (Philip, 2010), fruits (Kumar, Smita, Cumbal, Debut, Camacho, et al., 2015), seeds (Otari, Patil, Ghosh, & Pawar, 2014), oil (Kumar, Smita, Cumbal, & Debut, 2014b), bark (Sathishkumar et al., 2009), biomass (Kumar, Smita, Cumbal, & Debut, 2014c), and roots (Sreekanth, Ravikumar, & Eom, 2014) have already been reported in the literature. Since ancient times, both primary and secondary metabolites of plants (phytochemicals) have demonstrated their importance in human health applications, but the use of phytochemicals for the synthesis of metal nanoparticles still remains unexplored and is an area of great research potential.

The Capuli (*Prunus serotina* Ehrh. var. Capuli) cherry (Fig. 1(a)) is one of the most common fruits available on the highlands of Ecuador, Peru, Colombia, and Venezuela from December to February. It is similar in shape and taste to the black and Bing cherries. Its thin peel is reddish-purple with a slightly bitter taste, and the pulp is green. It is mostly eaten fresh, stewed, preserved, or made into jam or wine (Dugo, Mondello, Errante, Zappia, & Dugo, 2001). Its major phytochemical components include chlorogenic acid ((+)-catechin and (−)-epicatechin), proanthocyanidin (cyanidin-3-O-glucoside and cyanidin-3-O-rutinoside), and flavonol glycosides (quercetin-3-xyloside, quercetin-3-arabinoside) (Vasco, Riihinen, Ruales, & Kamal-Eldin, 2009).

Recently, there has been remarkably rapid progress in the development of photocatalytic reactions sensitized by high-brightness light-emitting diodes (LEDs). Several advantages are associated with the use of LED lamps as a light source, such as localized surface plasmon resonance enhancement (Gu, Qiu, Zhang, & Chu,

* Corresponding author. Tel.: +593 2 3989492.
*E-mail address:* krmbraj@gmail.com (B. Kumar).

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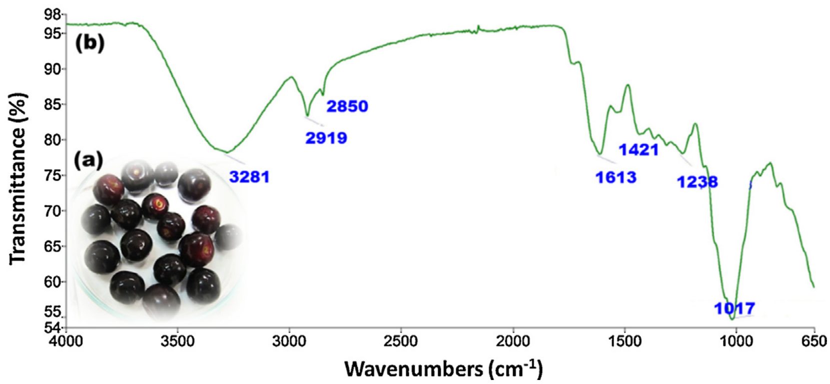


**Fig. 1.** (a) Photograph of Capuli cherries and, (b) the FTIR spectrum of the Capuli cherry extract.

2011), morphology and optical properties control (Stamplecoskie & Scaiano, 2010), improved membrane performance (Li, Verbiest, Strobbeb, & Vankelecom, 2014), high photon efficiency, low voltage of electricity, power stability, accuracy and low cost (Yeh, Wu, & Cheng, 2010). Owing to the high importance of and advances in the application of LEDs in photocatalytic reactions, we study the synthesis of AgNPs using blue LED light.

The green synthesis of differently shaped and sized AgNPs using plant materials has already been indicated by our group (Kumar, Smita, Cumbal, Debut, & Pathak, 2014, Kumar et al., 2014a, 2014b, Kumar, Smita, Cumbal, Debut, Camacho, et al., 2015), so the main objective of the present study is to compare the synthesis of Ag nanospheres using Capuli cherry extract (CCE) in the presence of white solar and blue LED light. In this work, the CCE acts as a reducing and capping agent, whereas the white solar and blue LED light activates the AgNP synthesis. The CCE and AgNPs are further characterized by Fourier transform infrared (FTIR) spectroscopy, ultraviolet–visible (UV–Vis) spectroscopy, hydrodynamic particle size analysis, transmission electron microscopy (TEM), and X-ray diffraction (XRD). The antioxidant efficacy of the AgNPs is also evaluated using 1,1-diphenyl-2-picrylhydrazyl (DPPH•) to determine whether these nanoparticles can be exploited as an antioxidant carrier source.

## Material and methods

### *Synthesis of AgNPs*

Silver nitrate ($AgNO_3$, 99.5%) was purchased from Spectrum, USA, the 1,1-diphenyl-2-picrylhydrazyl (DPPH•, >99.5%) was purchased from Sigma Aldrich, USA, and Milli-Q® water was used in all experiments. Fresh Capuli cherries were collected from the open market near Universidad de las Fuerzas Armadas-ESPE, Sangolqui, Ecuador; after thoroughly washed, Capuli cherries (50 g) were chopped and ultrasonicated in 100 mL of water for 10 min. For ultrasonication, ultrasonic transducer (DAIGGER GE 505, 500 W, 20 kHz) was immersed directly into the reaction solution and set to operate at timed pulses of 30 s on and 30 s off with a pulse amplitude of 72% at 25 °C for 10 min (5 min × 2). After ultrasonication, the purple-brown colored CCE was filtered using Whatman No. 1 paper and stored at 4 °C for further use. For green synthesis, 1.0 mL of the CCE was mixed with 10 mL of 1 mM $AgNO_3$ solution, and either kept in white solar light (65–80 cd/$m^2$) at 23–28 °C for 96 h, or in blue LED light (12 V, 0.26–0.28 A) at 25–48 °C for 8 h. The reaction mixtures were monitored at different time intervals. A clear suspension of AgNPs was subsequently prepared by centrifuging the reaction mixture containing the AgNPs at 5000 rpm for 20 min at 22–25 °C, and was then used in the instrumental analysis.

### *DPPH• assay*

The scavenging activity of the AgNPs at different time intervals was measured using DPPH• as a free radical model and implementing a method adapted from Kumar et al. (2015) and Kumar, Smita, Cumbal, and Debut (2015). An aliquot of CCE, AgNPs or $H_2O$ as control (1.0–0.2 mL) and $H_2O$ (1.0–1.8 mL) was mixed with 2.0 mL of 0.2 mM (DPPH•) in 95% ethanol. The mixture was vortexed vigorously and allowed to stand at room temperature for 30 min in the dark. Absorbance of the mixture was measured spectrophotometrically at 517 nm, and the free radical scavenging activity was calculated using the relation:

$$\text{Scavenging effect } (\%) = \left[1 - \frac{\text{absorbance of sample}}{\text{absorbance of control}}\right] \times 100 \qquad (1)$$

The scavenging percentage of all of the samples were plotted, and the final result was expressed as the % of DPPH• free radical scavenging activity (mL).

### *Characterization of AgNPs*

FTIR attenuated total reflection spectra were recorded on a Spectrum Two IR spectrometer (Perkin Elmer, USA) to detect the different functional groups in the CCE involved in nanoparticle synthesis. The synthesized AgNPs were characterized with a UV–Vis single-beam spectrophotometer (GENESYS™ 8, Thermo Spectronic, UK), while the hydrodynamic size distributions of the nanoparticles were analyzed using a dynamic light scattering (DLS) instrument (LB-550, Horiba, Japan). Transmission electron microscope (TEM) images and selected area electron diffraction (SAED) patterns were recorded digitally (Tecnai G2 Spirit TWIN, FEI, Holland). X-ray diffraction (XRD) studies on thin films of the nanoparticle were carried out using a diffractometer (EMPYREAN, PANalytical) and a $\theta$–$2\theta$ configuration (generator–detector), wherein a copper X-ray tube emitted a wavelength of $\lambda$ = 1.54 Å. Thermo gravimetric analysis (TGA) and differential thermal analysis (DTA) were carried out (TGA Q 500, TA Instruments, USA) by heating 5–10 mg of the sample up to 500 °C in a platinum sample cup at the rate of 20 °C/min.

## Results and discussion

### *FTIR analysis of CCE*

FTIR analysis was used to determine the functional groups present in the CCE (Fig. 1(b)). The broad band seen at 3281 $cm^{-1}$ reveals the presence of an —OH group, resulting from either alcoholic or polyphenolic stretching (Kumar, Smita, Cumbal, Debut, Camacho, et al., 2015), while the peaks around 2919 and 2850 $cm^{-1}$