Phytosynthesis of gold nanoparticles using Andean Aji’ (Capsicum baccatum L.)

Brajesh Kumar, Kumari Smita and Luis Cumbal

Cogent Chemistry (2015), 1: 1120982
MATERIALS CHEMISTRY | SHORT COMMUNICATION

Phytosynthesis of gold nanoparticles using Andean Ají’ (Capsicum baccatum L.)

Brajesh Kumar1*, Kumari Smita1 and Luis Cumbal1

Abstract: This article covers the importance of Andean Ají’/Chilli (Capsicum baccatum L.) mediated synthesis of gold nanoparticles (AuNPs), which favors for green chemistry and escape us from the use of hazardous chemicals. UV–visible spectroscopy was used to monitor the quantitative formation of AuNPs. Further, as synthesized AuNPs were characterized using Transmission electron microscopy, Dynamic Light Scattering, and X-ray diffraction. It produced spherical AuNPs at λmax = 540 nm of average size 23.9 ± 9.7 nm without any aggregation. Ají’ extract (aq) was the good reducing and capping agent in terms of conversion to Au3+ to AuNPs. The synthesized AuNPs, also enhancing the photocatalytic degradation of methylene blue (>50%, k = 1.9585 × 10−3 min−1) under direct solar light irradiation. In addition, the experimental approach is benign, ecofriendly, and inexpensive for industrial-scale production of nanoparticles using Ají extract as natural bioreductant.

Subjects: Analytical Chemistry; Environment & Agriculture; Material Science; Materials Chemistry

Keywords: phytosynthesis; Ecuadorian chilli; Capsicum baccatum L.; UV–vis; TEM; XRD; photocatalyst

1. Introduction

Nanotechnology and Nanoscience that deal with features as small as 10−9 m began to enter into mainstream physical sciences and engineering some 20 years ago. The most important challenge is to achieve 100% selectivity of the desired product molecule and develop renewable energy-based processes. Nanoparticle (NP) assemblies with controlled size, shape, and composition became

ABOUT THE AUTHOR

Dr. Brajesh Kumar is currently working as a Prometeo Researcher in the Centro de Nanociencia y Nanotecnología, Universidad de las Fuerzas Armadas - ESPE, Ecuador. He received his MSc and PhD in Chemistry from the University of Delhi, Delhi, India. His research interest is the development of sustainable and ecofriendly technique for natural product extraction, purification and analysis, plant mediated synthesis of nanoparticle and their applications for environmental remediation, active films of organic solar cells, nanomedicine, sensors; natural polymers, peptide chemistry, microwave and ultrasound assisted organic synthesis. He worked as a faculty member in different universities in India, South Korea and published several SCI/SCIE indexed research articles, patents and conference papers.

PUBLIC INTEREST STATEMENT

Plant-mediated synthesis of nanoparticles has attracted more attention, due to its simplicity, inexpensive and ecofriendliness nature. The formed gold nanoparticles using Andean Ají’/chilli were characterized by different analytical instruments and exhibited enhanced photocatalytic activity for the degradation (>50%, k = 1.9585 × 10−3 min−1) of methylene blue dye. We hope this study opens new scope in the field of nanoparticles synthesis and environmental remediation.
model catalysts and we used metal single crystals for decades (Narayanan & El-Sayed, 2005). Production of nanoparticles can be achieved through different methods, for example, reduction in solutions, chemical and photochemical reactions in reverse micelles (Cheng et al., 2011), electrochemical (Hirsch et al., 2005), thermal decomposition (Jen-La Plante, Zeid, Yang, & Mokari, 2010), sonochemical (Kumar, Smita, Cumbal, & Debut, 2015b; Korotchenkov et al., 2005), microwave assisted (Nadagouda, Speth, & Varma, 2011), and recently via biological routes. Biological methods for NPs synthesis using micro-organisms (Sunkar & Nachiyar, 2012), enzyme (Schneidewind et al., 2012), and plant or plant extract offer numerous benefits over chemical and physical methods. It is cost-effective, environmentally friendly, easily scaled up for large-scale synthesis; and there is no need to use high pressure, energy, temperature, and toxic chemical that may have an adverse effect on the medical applications (Joe & Beom, 2009; Kouvaris et al., 2012; Kumar, Smita, Cumbal, & Angulo, 2015; Kumar, Smita, Cumbal, & Debut, 2015a; Sivakumar, Nethra Devi, & Renganathan, 2012). Synthesis of NPs using plants (phytosynthesis) that secrete the functional molecules for the reaction is compatible with the green chemistry principles: (1) ecofriendly as are (2) the reducing agent employed, and (3) the capping agent in the reaction. There are some examples of phytosynthesis of NPs, including the use of live alfalfa for silver (Ag) and gold NPs (AuNPs) (Gardea-Torresdey et al., 2003), Plukenetia volubilis oil (Kumar, Smita, Cumbal, & Debut, 2014a) and leaf extract for AgNPs (Kumar, Smita, Cumbal, & Debut, 2014b), germinating chickpea seeds for CaCO3 crystals (Rautaray, Sanyal, Bhard, Ahmad, & Sastry, 2005), Citrus paradisi peel extract for ZnO NPs (Kumar, Smita, Cumbal, & Debut, 2014c), Rubus glaucus leaf and fruit extract for CuO NPs (Kumar, Smita, Cumbal, & Debut, in press), Passiflora tripartita fruit FeNPs (Kumar, Smita, Cumbal, Debut, & Angulo, in press), edible mushroom extract for Au, Ag, and Au–Ag NPs (Philip, 2009), flower extract of Lantana camara and the broth of lemongrass leaf for AuNPs (Kumar, Smita, Cumbal, in press; Shankar, Rai, Ahmad, & Sastry, 2005).

Chilli peppers have been a part of the human diet worldwide since at least 7500 BC. There is archaeological evidence at sites located from the Bahamas to southern Peru that chili peppers were domesticated more than 6,000 years ago, (Perry et al., 2007) and were one of the first self-pollinating crops cultivated in Central and South America (Bosland, 1996). Capsicum baccatum L. (Aji Amarillo) is a traditional vegetable crop in Ecuador, Argentina, Bolivia, Brazil, Chile, Peru, Costa Rica, Hawaii, and is also cultivated in many countries. It is utilized in Andean cuisine and is an essential part of the ethnobotanical knowledge of the region due to the presence of many bioactive compounds, such as capsaicinoids, phenolic compounds, carotenoids, protein/enzymes, polysaccharides, amino acids, and vitamins (Li et al., 2007; Rodríguez-Burruezo, Prohens, Raigón, & Nuez, 2009; Zimmer et al., 2012).

In the past years, few works have reported for the synthesis of SeNPs (Li et al., 2007) and AgNPs (Jha & Prasad, 2011; Li et al., 2007; Mendoza-Reséndez, Núñez, Barriga-Castro, & Luna, 2013) using extracts of the chili peppers. To the best of our knowledge, there are no reports on the synthetic capacities of C. baccatum or Aji for the synthesis of AuNPs. In this study, we discussed the synthesis of AuNPs using C. baccatum extract (aq) and as synthesized AuNPs were further characterized by UV–vis spectroscopy, Transmission electron microscopy (TEM), Dynamic Light Scattering (DLS), and X-ray diffraction (XRD) techniques. We also investigated the use of AuNPs for the photocatalytic degradation of methylene blue (MB) without using an additive reducing agent in solar light.

2. Experimental

2.1. Materials and synthesis of AuNPs

All chemicals were of analytical grade and used without any purification. Gold chloride hydrate (HAuCl4·xH2O 99.99%) was purchased from Aldrich (USA). MB (99.5%) was purchased from the Spectrum (USA) and Milli-Q water was used in all experiments. Fresh C. baccatum or Aji fruit was purchased from the popular market near Universidad de las Fuerzas Armadas ESPE, Sangolqui, Ecuador. After being washed thoroughly, Aji fruit (5 g) was cut finely and stirred (23–25°C) in 50 mL of deionized water for 120 min. After cooling, the light yellow color Aji extract was filtered using
Whatman No.1 paper and stored at 4°C for further use. For the extracellular phytosynthesis of AuNPs, 3 mL of extract was mixed with 10 mL of HAuCl₄ (0.5 mM) solution at room temperature (22–25°C). Reduction occurs rapidly as indicated by the appearance of purple-pink color after 60 min and studied the formation of the AuNPs at different time interval.

2.2. Photocatalytic degradation activity
In order to evaluate the photocatalytic performances of Au NPs, photocatalytic degradation of MB under solar light irradiation (1,000–1,150 cd/m²) was performed. In the reaction set 1, 5 mL of MB (10 mg/L) was mixed with 1 mL H₂O and another set 2, 5 mL MB (10 mg/L), AuNPs (500 μL) and H₂O (500 μL) were mixed in the dark (20 min) to reach an adsorption desorption equilibrium. Then both sets were kept in the direct sunlight and progress of the degradation reaction was monitored at different time intervals by measuring the absorption of MB in the filtrate at the wavelength 664 nm, before and after degradation using a UV–vis absorption spectrometer. Photocatalytic degradation % of MB was calculated using equation (1) and catalytic efficiency of the AuNPs was quantified by calculating the respective first-order rate constants (k) according to the Equation (2).

\[ \eta = \frac{A_0 - A_t}{A_0} \times 100\% \]  
\[ \ln \frac{A_0}{A_t} = kt \]

where \( \eta \) is the rate of degradation of MB in terms of percentage, \( A_0 \) is the initial absorbance of the dye solution and \( A_t \) is the absorbance of the MB at time \( t \).

2.3. Characterization of AuNPs
The UV–vis spectrum was measured using a spectrophotometer (Thermo Spectronic, GENESYS™ 8, England). Size and selective area electron diffraction (SAED) pattern of nanoparticles are studied on TEM (FEI, TECNAI, G2 spirit twin, Holland). The particle size distributions of nanoparticles were determined using the HORIBA, DLS Version LB-550 program. XRD studies on thin films of the nanoparticle were carried out using a BRUKER D8 ADVANCE brand \( \theta-2\theta \) configuration (generator-detector) X-ray tube copper \( \lambda = 1.54 \) Å, and LYNXEYE PSD detector.

3. Results and discussion

3.1. Visual and UV–vis analysis
The reaction of Au³⁺ ions with C. baccatum extract with time is displayed in Figure 1. The appearance of the purple-pink color indicated the feasibility of a reaction and the formation of AuNPs. This change of solution color may be attributed to the surface plasmon resonance (SPR) of the AuNPs and
provided a convenient spectroscopic signature of their formation (Kumar, Smita, & Cumbal, in press; Philip, 2009). Recent results with *C. annuum* extract reported by Li et al. (2007) indicated that the proteins which have amine groups played a reducing and controlling role during the formation of AgNPs in the solutions, and that the secondary structure of the proteins changed after reaction with Ag+. The absorbance of the reaction solution increases gradually with the appearance of two new peaks at 360 and 540 nm, whereas *C. baccatum* extract (aq) didn’t show any peak in the range of 400–800 nm. The peak at 540 nm corresponds to the SPR for AuNPs whereas the additional peak observed at 340–360 nm can be assigned to phytochemicals associated gold clusters, via intermediates, build up metallic AuNPs (Kumar, Smita, & Cumbal, in press).

### 3.2. TEM and DLS analysis

TEM images of the AuNPs are presented in Figure 2. It is evident that the AuNPs prepared using *C. baccatum* extract was mainly spherical with particle sizes in the range of 8–35 nm. As seen in TEM images, there was a layer of *C. baccatum* extract, but not any aggregates formed and AuNPs were highly dispersed. It may be due to the presence of the repulsive nature of the capping and stabilizing agent coated on the surface of AuNPs. SAED analysis carried out from a spherical AuNPs indicated the arrangement of circular bright spots, typically of the face-centered cubic (fcc) crystal system of elemental gold (Shankar et al., 2004).

### 3.3. DLS analysis

The hydrodynamic size distribution of AuNPs was determined by the DLS method (Figure 3). The average particle sizes of AuNPs were found to be 23.9 ± 9.7 nm with polydispersity index (PDI) = 0.1647. PDI > 0.1, clearly indicates that as synthesized AuNPs were polydispersed in nature. Interestingly, the average particle sizes determined by DLS method were slightly higher than those measured by TEM study. This is because (1) the phytochemicals formed a shell around the AuNPs, (2) small particles were screened by the bigger one (Kumar, Angulo, Smita, Cumbal, & Debut, in press), and water absorption on electrostatic stabilized particles (Das, Roy, Mondal, Bera, & Mukherjee, 2013).

![Figure 2. TEM images of AuNPs synthesized in solution with reaction times of 72 h.](image)

![Figure 3. DLS size distribution of the AuNPs.](image)
3.4. XRD analysis

Figure 4 shows the XRD spectrum corresponding to AuNPs and confirmed its crystalline nature. The Bragg reflection peaks observed at 37.95°, 44.04°, and 64.53° correspond to the (1 1 1), (2 0 0), and (2 2 0) planes (Ref No. 00-004-0784). The strongest peak at 37.95° attributed to the predominant growth of crystal lattice of AuNPs in the direction of (1 1 1) plane, whereas one reflection observed at 31.50° corresponds to the bio-organic phase as an impurity. All the three characterization peaks for AuNPs reveal that they are crystallized in (fcc) structure (Philip, 2009; Shankar et al., 2005). The obtained results were well supported with the data obtained from UV–vis and SAED studies.

3.5. Photocatalytic activity

The kinetics of the photocatalytic degradation of MB using AuNPs followed by UV–vis spectroscopy is shown in Figure 5. The obtained percentage degradation of the MB with AuNPs at 300 min solar light exposure is 50.90% (Figure 5(a)). This reveals that AuNPs act as an electron transfer mediator between the unreacted phytochemicals of C. baccatum and MB by acting as a redox catalyst via electron relay effect (Kumar et al., 2014a). The decrease in intensity of absorption corresponding to MB around 664 nm is monitored as a function of time. The kinetic data well fits in the first-order rate Equation (2) with the rate constant ($k$) = 1.9586 × 10$^{-3}$ min$^{-1}$ and the linear plot as shown in Figure 5(b). Therefore, as-prepared AuNPs could also be used as an effective sunlight active photocatalyst.

4. Conclusion

In conclusion, AuNPs has been successfully synthesized using C. baccatum extract as reducing and capping agents. Various analytical techniques, including UV–visible, TEM, DLS, and XRD results confirmed that the AuNPs were spherical, highly dispersed, 23.9 ± 9.7 nm of average size and crystalline. As-synthesized AuNPs also exhibited an efficient photocatalytic activity in the degradation of MB.
(>50%, \( k = 1.9585 \times 10^{-1} \text{ min}^{-1} \)) under direct solar light irradiation. Therefore, the proposed approach could provide information about the potential utility of \( C. \) baccatum as an inexpensive, clean, and cost-effective raw material source for the synthesis of AuNPs.

Acknowledgments

We thank Ing. Sara Guerra, ESPE for the TEM measurements and Dr. Colon Velasquez, INIGEMM for providing XRD instrumental assistance.

Funding

This scientific work has been funded by the Prometeo Project of the National Secretariat of Science, Technology and Innovation (SENESCYT), Ecuador.

Author details

Brajesh Kumar1

E-mails: krmbraj@gmail.com, bkumar@espe.edu.ec

ORCID ID: http://orcid.org/0000-0002-0557-9790

Kumari Smita

E-mail: kumarismi@gmail.com

Luis Cumbal1

E-mail: lccumbal@espe.edu.ec

1 Centro de Nanociencia y Nanotecnología, Universidad de las Fuerzas Armadas - ESPE, Av. Gral. Rumiñahui s/n, P.O. Box 171-5-231B, Sangolquí, Ecuador.

Citation information

Cite this article as: Phytosynthesis of gold nanoparticles using Andean Ají (Capsicum baccatum L.)., Brajesh Kumar, Kumari Smita & Luis Cumbal, Cogent Chemistry (2015), 1: 1120982.

Cover image

Source: Authors.

References


