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# Electrochemical and spectral characterization of silver nanoparticles synthesized employing root extract of *Curculigo orchioides*

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A facile eco-friendly approach is employed to prepare silver nanoparticles, using root extract of *Curculigo orchioides* (family Hypoxidaceae). The aqueous solution of silver ions in contact with root extract of *Curculigo orchioides* are reduced to zero valent silver and eventually stabilized as silver nanoparticles. An electrochemical approach has been presented to characterise conversion of silver ions into metallic silver in solution. A significant change in cyclic voltammetric characteristics has been observed to mark the transition of metal ion from higher oxidation state to stabilized silver in zero oxidation state. UV-Vis, FTIR, and X-ray diffraction analyses and atomic force microscopy supports the formation of spherical silver nanoparticles within 40 min of reaction time at room temperature.

**Keywords:** Biosynthesis, Root extract, *Curculigo orchioides*, Electrochemical monitoring, Silver nanoparticles

Nanosilver finds numerous applications in varied areas including spectrally selective coating for solar energy absorption, intercalation materials for electrical batteries, optical receptors catalysis in the chemical reactions and bio-labelling, antimicrobial agent for safe water, food packaging, wound dressings etc. due to its unique electronic, optical, chemical and biochemical properties.

Scientists have long been exploring the biomimetics approaches adopted by Nature to create the functional structures through nanosynthesis[1,2]. The era of biosynthesis of nanoparticles began with the report on intracellular biosynthesis of nanosized magnetite by iron reducing bacteria[3,4] which continued growing using yeasts cells[5], actinomycetes[6], fungi[7,8] and more recently trend of extracellular biosynthesis using extracts/broth from different parts of plants as an attractive approach. The extracellular bio-nanosynthesis, employing renewable phytoresources represents an environmentally benign, clean, green and rapid approach of nano particle synthesis. Among biogenic nano particles, nano silver occupies a special place due to its inhibitory effect towards various microorganisms commonly present in clinical, domestic and industrial environment[2]. Various parts of plants extracts have been explored for the purpose of silver nanoparticle synthesis using silver ions as substrates. A mini review of literature has been included in Table 1 showing representative examples of leaves, fruits, flowers, stem, bark, latex and roots extracts as phytoresources for extracellular biosynthesis of silver nano particles. Literature survey reveals that use of leaf extract[9-28] predominates over extracts of other parts of plants such as stem[30,31] , bark[32-34] , seed[33], flowers[35,36], fruits[37-41], roots[30,42-47] for extracellular nano synthesis, and the characterisation involved UV-Vis spectroscopy, FTIR spectroscopy, X-ray diffraction and transmission electron microscopy, however not much has been reported about electrochemical approach to characterise the nanoparticles.

*Curculigo orchioides* (family Hypoxidaceae, common name Kali musli), is a herbaceous, tuberous geophillous, perennial plant, widely distributed all over India. Roots of *Curculigo orchioides* are well known for their medicinal value and are rich source of alkaloids, glycosides, saponins and sterols[50,51]. Present paper reports a facile eco-friendly approach for preparing silver nanoparticles using root extract of *Curculigo orchioides*. An electrochemical approach has been suggested to characterise conversion of silver ions into metallic silver in solution along with UV-Vis spectroscopy, FTIR spectroscopy, X-ray diffraction analyses and atomic force microscopy of biogenic silver nanoparticles.

Table 1 — Phytoresources for extracellular biosynthesis of silver nano particles.

| Phytoresource | Shape of silver NPs | Size range/ average size (nm) | Reference & year |
|---|---|---|---|
| **Leaf extract** | | | |
| *Aloe vera* | Spherical | 10-20 | Chandran *et al.*[9] 2006 |
| *Azadirachta indica* | Spherical | 5-35 | Shankar *et al.* [10] 2004 |
| | Core-shell Ag-Au | 50-100 | |
| *Capsicum annum* | Spherical | 8-12 | Li *et al.* [11] 2007 |
| *Cinnamomum camphora* | Triangular | 55-80 | Huang *et al.*[12] 2007 |
| *Coriandrum sativum* | Spherical | 8-75 | Sathyavathi *et al.*[13] 2010 |
| *Germanium Aqueous extract* | Quasi linear superstructures | 16-40 | Shankar *et al.*[10] 2003 |
| *Mangolia kobus* | Spherical | 15-500 | Song *et al.*[14] 2009 |
| *Diopyros kaki* | | | |
| *Ginkgo biloba* | | | |
| *Pinus desiflora* | | | |
| *Platanus orientalis* | | | |
| *Mentha piperata* | Face centred cubic Crystalline | 5-50 | Parashar *et al.*[15] 2009 |
| *Syzium cumini* | Spherical | 30 | Kumar *et al.*[16] 2010 |
| *Eucalyptus hybrida* | Cubical | 50-150 | Dubey *et al.*[17] 2009 |
| *Acalypha indica* | | 20-30 | Krishnaraj *et al.*[18] 2010 |
| *Argemone maxicana* | Cubic and Hexagonal | 10-50 | Singh *et al.*[19] 2010 |
| *Allium cepa* | Spherical | 33.67 | Saxena *et al.*[20] 2010 |
| *Euphorbia hirta* | Spherical | 40-50 | Elumalai *et al.*[21]2010 |
| *Murraya koenigii* | Spherical | 10 -20 | Phillips *et al.*[22] 2011 |
| *Cassia auriculata* | polydispersed spherical | 20- 40 | Udayasoorian *et al.*[23] 2011 |
| *Catharanthus roseus* | Face centred cubic structure | 35-55 | Ponarulselvam *et al.* [24] 2012 |
| *Ocimum tenuiflorum* | face centred cubic structure | 25-40 | Patil *et al.* [25] 2012 |
| *Coleus aromaticus* | Spherical | 44 | Vanaja & Annadurai[26] 2013 |
| *Citrullus colocynthis* | Spherical | 31 | Satyavani *et al.* [27] 2011 |
| *Curculigo orchioides* | Spherical | 5 to 17 | Venkatachalam *et al.*[28] 2016 |
| **Stem/bark/latex extract** | | | |
| *Jatropha curcas* (latex) | Crystalline | 10-20 | Bar *et al.*[29] 2009 |
| Ocimum sanctum *(stem)* | Spherical | 3.5-5.6 | Ahemad *et al.*[30] 2010 |
| *Desmodium triflorum (whole plant)* | Spherical | 05-20 | Ahemad *et al.*[31] 2011 |
| *Boswellia ovalifoliolata* and *Shorea tumbuggaia (*bark extracts*)* | Spherical | 30-40 | Savithramma *et al.*[32] 2011 |
| *Syzygium cumuni* (seed extract) | Cubic face centred | 93 | Banerjee & Narendhirakannan *et al.*[33] 2011 |
| *Cinnamomum zeylanicum (bark)* | -- | 30-150 | Gauthami *et al.*[34] 2015 |
| **Flower extract** | | | |
| *Achillea biebersteinii* | Hexagonal, pentagonal and spherical | 10-14 | Baharara *et al.*[35] 2014 |
| *Sonchus oleraceus* | Spherical | 12 -28 | El-sherbiny *et al.*[36] 2015 |
| **Fruit extract** | | | |
| *Emblica officinalis* | -- | 10-20 | Ankamwar *et al.*[37] 2005 |
| *Carica papaya* | Cubic structure | 15 | Jain *et* al.[38] 2009 |
| *Tanacetum vulgare* | -- | 16 | Dubey *et al.*[39] 2010 |
| Apple | Flower-like | 50 -300 | Umoren et al. [40] 2014 |
| *Carica papaya* | -- | -- | Firdaus *et al.*[41] 2017 |
| **Root / Tuber extract** | | | |
| *Ocimum sanctum.* | Spherical | 8-12 | Ahemad *et al.*[30] 2010 |
| *Curcuma longa* | FCC structure | 6.3±2.64 | Shameli *et al.*[42]2012 |
| *Morinda citrifolia* | Spherical to oval | 32–55 | Suman *et al.*[43] (2013) |

(*Contd.*)

Table 1 — Phytoresources for extracellular biosynthesis of silver nano particles. (*Contd*.)

| Phytoresource | Shape of silver NPs | Size range/ average size (nm) | Reference & year |
|---|---|---|---|
| *Daucus carota* (Black Gajar) | -- | 5-20 | Abubakar *et al*.[44] (2014) |
| *Justicia adhatoda* | -- | 25 | Ponvel *et al*.[45] (2015) |
| *Croton sparsiflorus* | Spherical | 30-50 | Joshi *et al*.[46] (2015), |
| *Mimosa Pudica* | Spherical | 35-40 | Sreenivasulu *et al*.[47] (2016) |
| *Curculigo orchioides* | Spherical | 50-70 | present report |
| **Plant derived compound** | | | |
| Apiin (from Henna leaf) | Quasi-spherical | 39 | Kasthuri *et al*.[48] 2009 |
| Phyllanthin (from *Phyllantyhus annus*) | Quasi-spherical to ellipsoidal | 30 | Kasthuri *et al*.[49] 2009 |

## Experimental Section

Dried roots of *Curculigo orchioides* were purchased from local market, identified in the Botany Department, J.N.V. University. All chemicals used in present study were from E. Merck (Mumbai, India). All the solutions were prepared in double distilled water. Cyclic Voltammograph (CV-27 BAS, USA) with a XY-2000 recorder (Houston Instrument Division, USA) was used to record the cyclic voltammograms (CV). Glassy carbon electrode ($A = 4.91\times 10^{-2}$ $cm^2$) was used as a working electrode; Ag/ AgCl electrode as reference electrode and a platinum wire fitted with C-1 cell stand (BAS, USA) served as a counter electrode. A UV-Vis spectrophotometer (Lambda 900, Perkin Elmer), FTIR spectrometer (Model 8101A, Shimadzu), X-ray Diffractometer (X'pert Pro, Netherlands) and Atomic Force Microscope (NT-MDI solver TS150, Ireland) were used for spectral and morphological characterisation. All the experiments were carried out at ambient temperature of 25±1°C.

### Extract preparation

The dried roots of *Curculigo orchioides* were ground to fine powder and extracted by boiling the powder in double distilled water (2 g/100 mL) in an Erlenmeyer flask for 60 min. under continuous stirring on a magnetic hot plate. The 2% extract (w/v) thus prepared was cooled, filtered and stored under refrigeration for further experiments.

### Synthesis of nanoparticles

A 100 mL aqueous $AgNO_3$ solution (1mM), was spiked with different volumes (1 to 20 ml) of the stock 2% root extract under continuous stirring on a magnetic stirrer, at room temperature. The bio-reduced silver nitrate solution was centrifuged at 10,000 rpm for 5 min., the residue-pellet formed at the bottom of centrifuge tube was washed thrice with distilled water to remove any free proteins/ enzymes from root extract and reserved for spectral and morphological investigations.

### Characterisation of nanoparticles

The electrochemical redox studies of $AgNO_3$/ $KNO_3$ (0.1 M) as supporting electrolyte, was carried out with and without plant extract by cycling the potential between +0.5 to -0.5 V vs Ag/AgCl electrode. The UV-Vis spectra of aliquot containing $AgNO_3$ and the root extract were recorded in the wavelength range 380-600 nm. To carry out the XRD measurements, sample solution was drop-coated onto a glass substrate. XRD pattern was recorded employing Cu–Kα1 radiation (λ=1.5406 Å); nickel monochromator filtering wave at tube voltage 40 KV; tube current 30 mA; in the region of 2θ from 0° to 80° at 0.02° $min^{-1}$ and the time constant was 2s. Further morphological features of silver solution were record using Atomic Force Microscopy in tapping mode.

## Result and Discussion

The potential of plant extracts to reduce various metal ions to their nano particle forms has been well documented. Silver nanoparticles exhibit a yellowish-brown colour in aqueous solution due to the excitation of surface plasmon in silver nanoparticles. In this direction, reductive potential of root extract of *Curculigo orchioides* has been investigated. The effect of spiking plant root extract to $AgNO_3$ solution was observed immediately as change in colour of aliquot started changing from colourless to greyish yellow to orange-brown and finally dark brown. Figure 1 shows 1mM aqueous silver nitrate solution without (A) and with (B), the root extract of *Curculigo orchioides* (0.2%). Distinct changes in solution from colourless to brown depict the existence of silver nanoparticles in flask B. The bio-reduction of $Ag^+$ to Ag NPs in solution was monitored by periodic sampling of aliquot and recording the UV-Vis spectra.

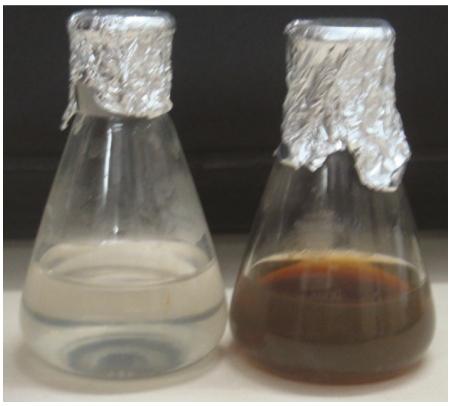

Fig. 1 — Flasks containing 1mM silver nitrate aqueous solution without (A) and with (B) *Curculigo orchioides* root extract (0.2%) after 45 min of reaction.

The UV-Visible spectra record (Fig. 2) of aliquots of silver nitrate solution spiked with root extract (0.2%), clearly shows a characteristic surface plasmon resonance absorption band with maximum absorption at 440 nm indicating the presence of silver nanoparticles. The intensity of the peak increases steadily as a function of time of reaction without any shift in the peak.

Electrochemical behaviour of $Ag^{+/0}$ was studied by carrying out cyclic voltammetry in the potential range +0.5 V to -0.5 V vs Ag/AgCl in a repetitive scanning mode at a scan rate of 10 $mV.s^{-1}$, consuming almost 200s for one cycle of forward cathodic and reverse anodic scan. CV characteristics of silver salt solution at zero min. (1st scan) i.e. immediately after spiking *C. orchioides* root extract (0.2%) and for 5 subsequent cycles are included in Table 2. Figure 3a, shows the record of cyclic voltammograms of 1mM silver salt solution in aqueous 0.1M $KNO_3$ medium, immediately after spiking *C. orchioides* root extract (0.2%) and A well defined redox signal with cathodic peak at -0.09 V ($E_{pc}$) and anodic peak at +0.17 V ($E_{pa}$) vs Ag/AgCl electrode corresponds to the electrochemical reduction of $Ag^+$ to $Ag^0$ during first cathodic scan and re-oxidation $Ag^0$ to $Ag^+$ during first anodic scan. CV scanning was continued for 5 more cycles, as revealed in Fig. 3b-f. The higher anodic current($I_{pa}$) as compared to cathodic current($I_{pc}$), appears to be due to oxidation of $Ag^0$ produced during cathodic reduction as well as those produced by biochemical reduction of $Ag^+$ giving rise to catalytic current along with electrochemical diffusion current (EC mechanism). Further, shift of anodic peak shifted towards more positive potential and marked decrease in peak current observed in subsequent cycles is also

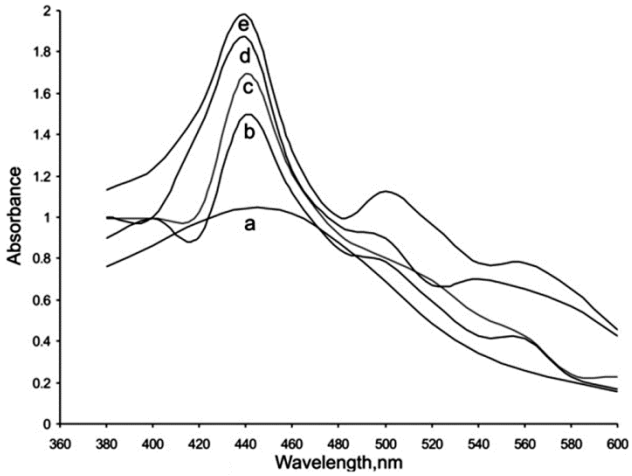


Fig. 2 — UV-Visible spectra of 1mM aqueous silver nitrate solution spiked with root extract of *Curculigo orchioides* (0.2%) with the reaction of time of 15 min (a), 20 min (b), 30 min (c), 40 min (d), 45 min (e).

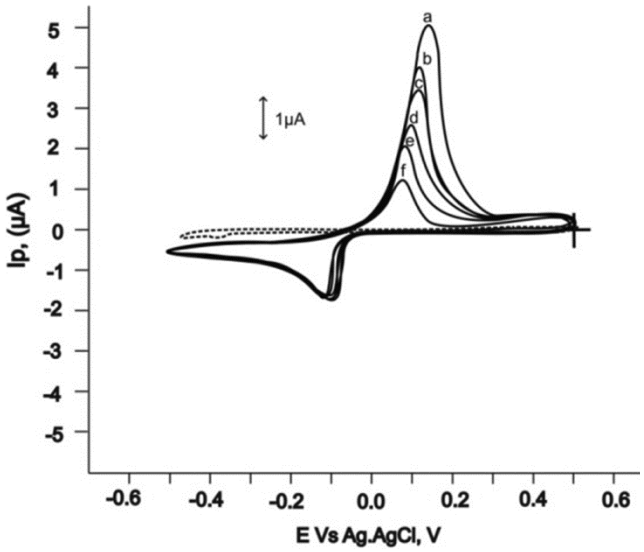


Fig. 3 — Cyclic voltammograms of *Curculigo orchioides* root extract reduced silver nanoparticles. 1mM $AgNO_3$ (metal salt) in 0.1M $KNO_3$ (supporting electrolyte) at GCE vs Ag/AgCl electrode at scan rate10 $mV.s^{-1}$. (a) 1st CV cycle just after spiking the root extract; (b to f) subsequent 2nd to 6th CV cycle.

Table 2 — Cyclic voltammetric characteristics of 1mM $AgNO_3$/0.1M $KNO_3$ spiked with *Curculigo* root extract (0.2%), GCE vs. Ag/AgCl electrode, scan rate 10 $mV.s^{-1}$.

| CV Scan cycle | $E_{pc}$, V | $E_{pa}$, V | $I_{pa}$/ $I_{pc}$ |
|---|---|---|---|
| 1st | -0.090 | +0.170 | 3.06 |
| 2nd | -0.085 | +0.170 | 2.60 |
| 3rd | -0.08 | +0.165 | 2.06 |
| 4th | -0.070 | +0.160 | 1.50 |
| 5th | -0.060 | +0.150 | 1.18 |
| 6th | -0.050 | +0.140 | 0.86 |

an indication of stabilized $Ag^0$ undergoing oxidation. This observation is in consistence with those reported by Kasturi *et al*.[49] for phyllanthin assisted nano silver synthesis. Cathodic peak parameters did not show any appreciable change in subsequent cycles, implies that reduced silver, $Ag^0$ is stabilized by plant root extract at electrode surface. The anodic current during first scan is almost three times than that of cathodic current; by 5th cycle $I_{pa}/ I_{pc}$ appears close to unity; and by 6th cycle $I_{pa}/ I_{pc}$ is less than unity, suggests the equilibrium state has reached within 20 min of introducing the root extract into the metal salt solution. UV-vis spectral studies also indicated initiation of formation of silver nanoparticles (Ag NPs) by 20 min and completion by 40 min of contact time at room temperature.

Chemical environment on the surface of the biogenic nanoparticles was probed in by FTIR spectroscopy. The FTIR spectrum of silver nanopowder synthesized using root extract is shown in Fig. 4. The broad band appearing at 3450 $cm^{-1}$ is assigned for O–H stretching vibration indicating the presence of phenolic–OH groups in the reducing medium. The strong intense peaks at 1377 and 1643 $cm^{-1}$ corresponds the amide I bands of proteins in the root extract. Small peaks in the region of 860-680 $cm^{-1}$ are due to presence of aromatic C-H bending. Peak at 1029 $cm^{-1}$ is attributed to the binding of $–OCH_3$ to the metal ion which is also in concordance with the reported affinity of methoxy group ($–OCH_3$) to metal ions[49,52]. The result of this FTIR spectroscopic study confirmed that plant extract used for present study has the ability to perform the dual functions of reduction of silver salt and stabilization of biogenic silver nanoparticles through methoxy group of xylopyranosyl β-glycopyranoside[51] as shown in inset of Fig. 4.

Figure 5 shows atomic force microscopic images of root extract reduced silver solution recovered after 40 min. of contact time at room temperature. Particles are well dispersed in the solution without aggregation in the range of 100-300 nm. The crystalline nature of silver nanoparticles was confirmed from the X-Ray diffraction analysis. The diffraction pattern peaks at

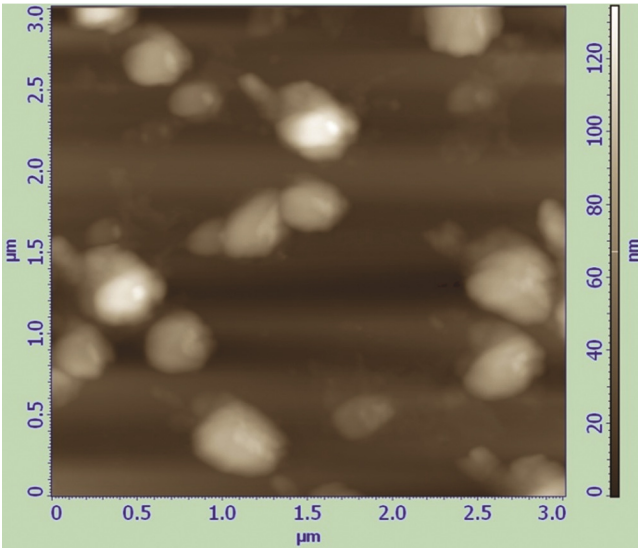


Fig. 5 — AFM image of *Curculigo orchioides* root extract reduced silver nanoparticles.

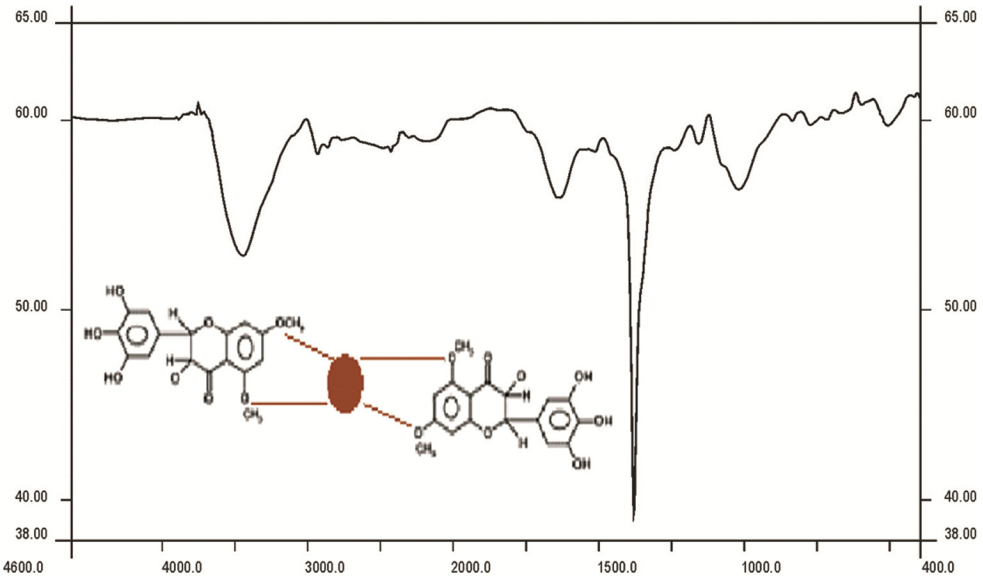


Fig. 4 — FTIR spectra of *Curculigo orchioides* root extract reduced silver nanoparticles.

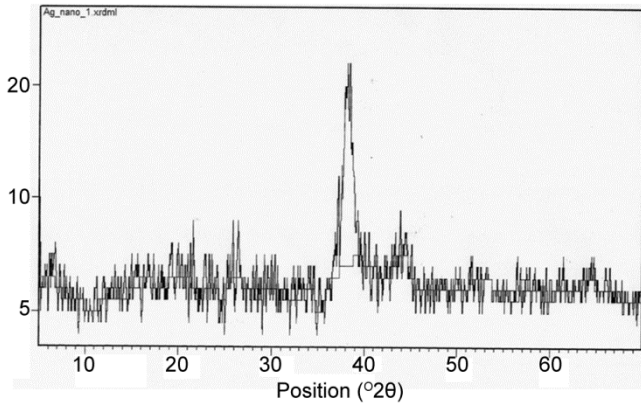


Fig. 6 — XRD pattern of biosynthesized silver nanoparticles.

38.1 and 44.5 and 64.6 corresponds to the (111), (200) and (220) facets of the face centred cubic crystal structure respectively. Figure 6 shows the XRD pattern of Ag nanoparticles obtained using *C. orchioides* root extract. The peak corresponding to the (111) plane is more intense than the other planes. The ratio between the intensity of the (200) and (111) diffraction peaks is much lower than the usual value (0.52) suggesting that the (111) plane is the predominant orientation. The biogenic nanoparticles can be used for various biomedical, pharmaceutical and biotechnological commercial applications.

## Conclusion

A facile and eco-friendly protocol has been proposed for biosynthesis of well dispersed crystalline, silver nanoparticles in the size range 100-300 nm, using *Curculigo orchioides* roots (rhizome) extract within 40 min. of reaction time at room temperature. The rate of silver nanoparticle synthesis using *Curculigo orchioides* extract is faster than the microbe mediated synthesis, while displaying all the characteristic features of nano size silver.

Nanoparticles are well dispersed in the solution without aggregation. The electrochemical characterizations performed by using cyclic voltammetry show significant responses for change in reduction potential of the metal ion from higher oxidation state to zero oxidation state.

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