

Green synthesis of cobalt oxide nanoparticles using *Polyalthia longifolia* leaves extract

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Abstract

Cobalt-oxide nanoparticles (Co₃O₄ NPs) were fabricated using *Polyalthia longifolia* leaves extract from cobalt acetate at room temperature. The synthesized Co₃O₄ NPs were explored using X-ray powder diffraction (XRD), scanning electron microscopy (SEM), energy-dispersive X-ray (EDX), Fourier transform infrared spectroscopy (FTIR), photoluminescence (PL) and UV-DRS techniques. The Co₃O₄ NPs were in highly uniform shape and size was in the size of 40-60 nm. In view of eco-benign and cost-effective nature, the present investigation revealed that *Polyalthia longifolia* could be used for the procurable synthesis of Co₃O₄ NPs.

Keywords: Green synthesis, Co₃O₄ NPs, *Polyalthia longifolia*

1. Introduction

Cobalt has different oxidation states, as well as a variety of coordinations. As a result of their mixed electronic valency of cobalt, stoichiometric and non-stoichiometric oxides, and/or the presence of oxygen vacancies, Co₃O₄ show a wide area for the formation of several frameworks. In contrast to other 3d transition metal oxides, Co₃O₄ have a multi-electronic valence and a rich coordination. This allows cobalt to exist in a variety of spin states in its oxide forms, including low, heavy, and intermediate spin. The physics of Co₃O₄ is appealing from a basic standpoint as well as in spintronic applications because of these possible spin states.

It is a multi-functional potent material with diverse practical applications, including electrochromic sensors, heterogeneous catalysis, pigments and dyes, anode materials in Li-ion rechargeable batteries, and energy storage devices [1-6]. It is an antiferromagnetic p-type semiconductor with diverse experimental applications. To make Co₃O₄ NPs, researchers used a variety of physical and chemical methods, including hydrothermal reaction, thermal decomposition of cobalt oxalate, microwave process, and thermal decomposition of sol-gel derived oxalates, solution combustion route, and combustion method [7-13]. Although these physical/chemical methods have proven to be very successful, they are complex and environmentally unfriendly due to the necessary energy balance and/or waste produced. Biosynthesis of Co₃O₄ NPs has never been recorded before, to our knowledge. However, it has been demonstrated that such an appealing green approach can be used to successfully synthesize metallic nanoparticles and some limited oxides [14-19].

The use of *Polyalthia longifolia* natural extract as an effective chelating agent for the simple and swift biosynthesis of pure Co_3O_4 NPs at room temperature is recorded for the first time in this article. Since no inorganic/organic solvents, surfactants, or high temperatures were used, this synthesis was a green and environmentally friendly operation.

2. Material and methods

2.1. Green synthesis of Co_3O_4 NPs

Leaf extracts were made by combining 100 ml deionized water with 3 g powdered plant leaves material and heating for 1 hour at 80 °C on a magnetic stirring hot plate. To eliminate solid residual waste, the extract solution was filtered three times with Whatmann filter paper. 6.0 g of the precursor salt, cobalt acetate was applied to 100 mL of filtered solution. After adding the precursor, the pH fell from 5.7 to 4.5. With gentle stirring, the solution was heated for 2 hours at 60 °C. After allowing the solution to cool to room temperature, the pellet was centrifuged (10,000 rpm/10 min) and washed three times with deionized water. To obtain highly crystalline pure phase Co_3O_4 NPs, the obtained pellet was dried at 100 °C for 2 hours before being annealed at 400 °C in open air.

2.2. Characterization techniques

Morphological analysis and elements mapping of the Co_3O_4 NPs were examined by scanning electron microscopy (SEM-VEGA3 TESCAN), and energy dispersive X-ray analysis (EDX) for elemental mapping were conducted using the same instrument. The crystal structure analysis of the Co_3O_4 NPs was analyzed by X-ray diffraction (XRD, Bruker, D8-Advanced Diffractometer). Diffuse reflectance spectrum (DRS) of Co_3O_4 NPs was conducted using UV-Vis Spectrophotometer (JASCO V-770). Chemical bonding interactions and functional groups were explored by Fourier transform infrared spectroscopy (FT-IR, 4600 Type A D044761786). Spectral analyses of photoluminescence (PL) of Co_3O_4 NPs were conducted on FP-8200 Spectrofluorometer.

3. Results and discussion

3.1. Morphological analysis

SEM was used to examine the morphology of the Co_3O_4 NPs, as shown in Fig. 1. The Co_3O_4 NPs were joined closely in the SEM pictures, forming aggregates with varying distances. The Co_3O_4 NPs were almost quasi-spherical in shape, with an average size of 40-60 nm. Due to magnetic induction between the particles, the aggregated NPs were adsorbed on the surface.

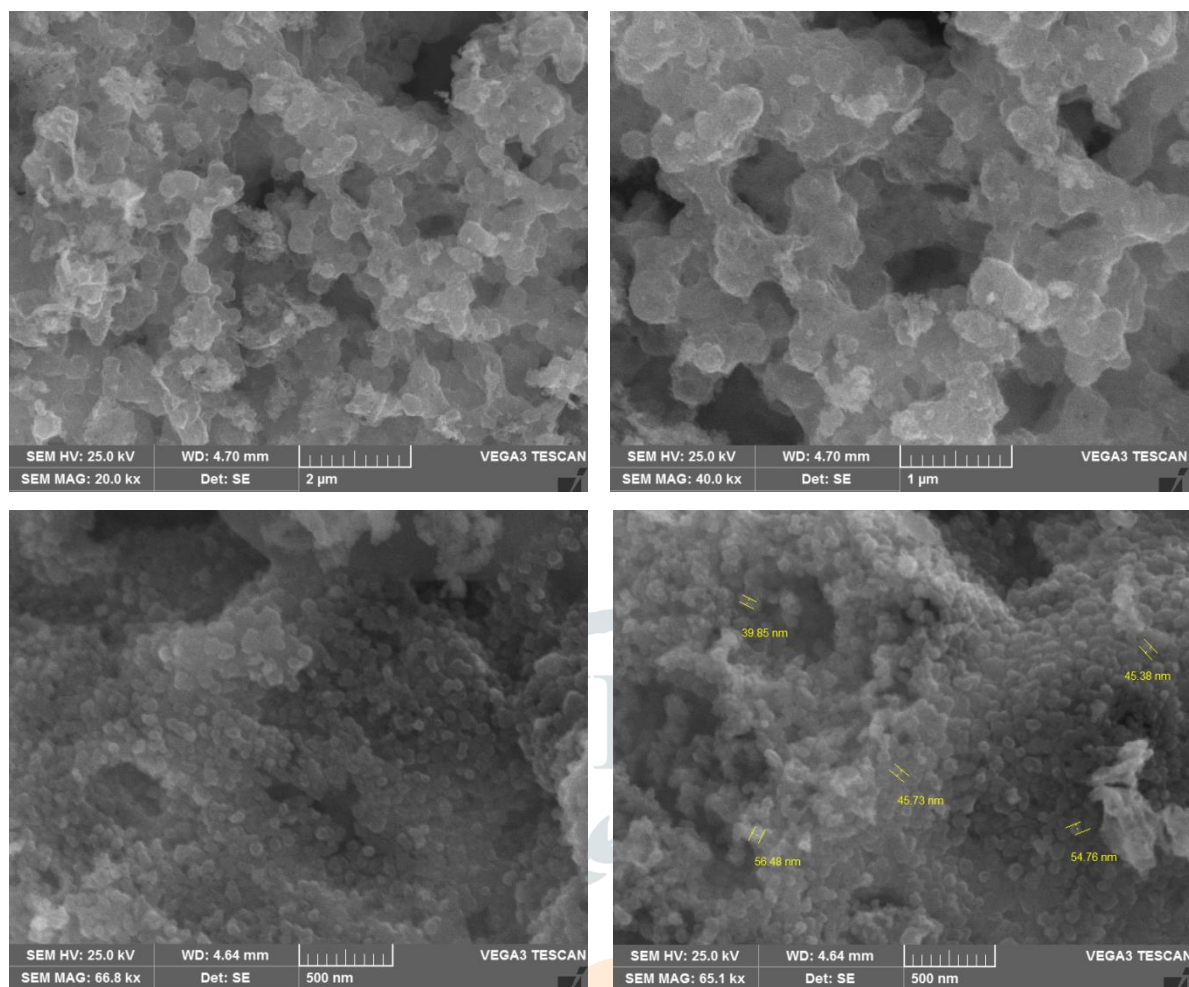


Fig. 1. SEM images of the Co_3O_4 NPs

3.2. Elemental composition

Figure 2 depicts a common EDX spectrum on a 400 °C annealed sample. Other than Cobalt and Oxygen, no other elements are detected. So far, no other element has been found, suggesting that the Co_3O_4 NPs following the preparation and final filtration protocol are chemically pure.

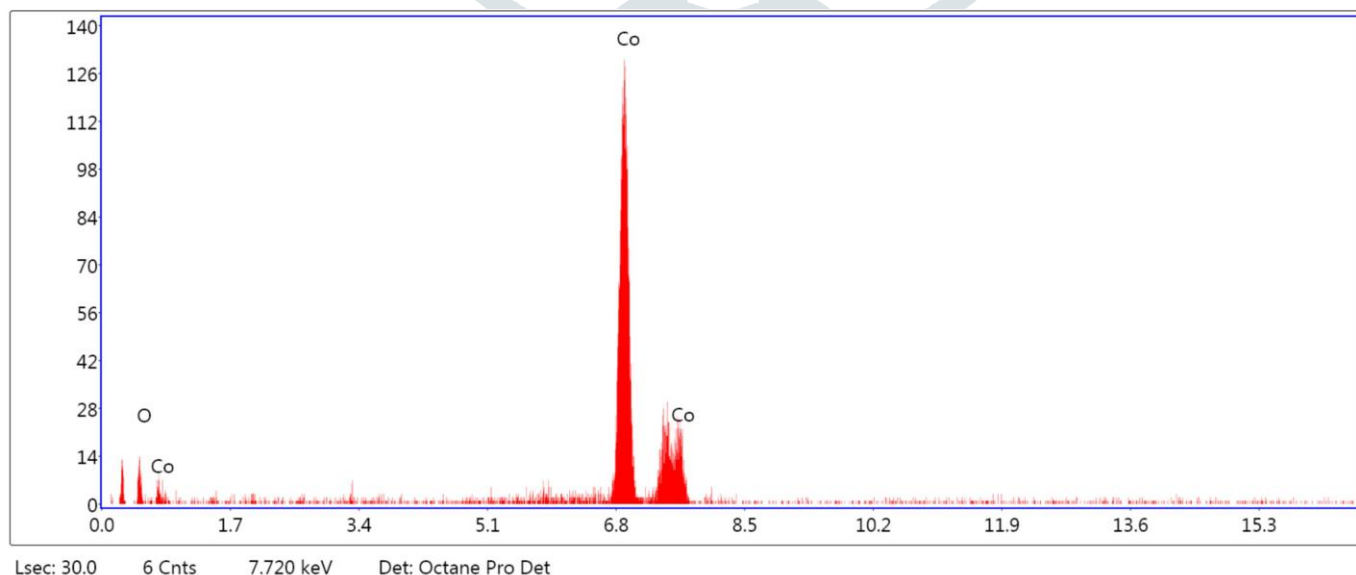


Fig. 2. EDX spectrum of Co_3O_4 NPs

3.3. Crystallographic study

Figure 3 depicts the XRD diffraction anatomy of Co_3O_4 NPs. All of the diffraction peaks indexed with Miller indices (311), (511), and (440) were obtained in the NPs that were annealed at 400 °C, and these peaks can be indexed to cubic phase pattern (JCPDS no 43–1003), and there is no additional peak, indicating that the synthesis of a single phase Co_3O_4 NPs was effective. Because of the rearrangement of the atomic structure of green synthesized NPs, the sharp apexes indicate that the particles are nanoscale and crystalline in nature, indicating that the dimension of the biosynthetic particles is fine and tiny.

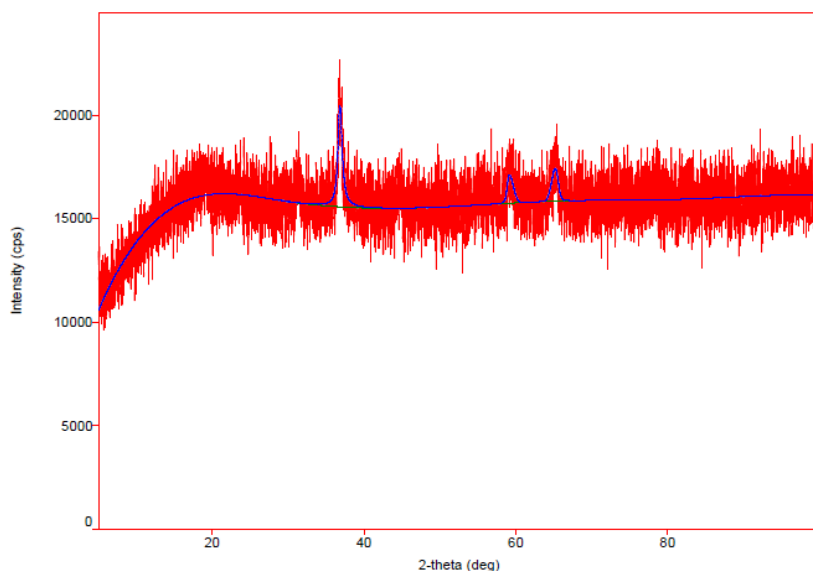


Fig. 3. XRD Spectrum of Co_3O_4 NPs

3.4. UV-DRS study

UV-DRS spectrometry was used to confirm the formation of Co_3O_4 NPs (Fig. 4). The absorption limit of the as-prepared Co_3O_4 NPs is 289 nm, which is the typical absorption peak of Co_3O_4 NPs. Phenolic compounds have a high affinity for metals due to the presence of carboxylic and hydroxyl groups. The hydrogen from the ortho position of the phenolic hydroxyl group is removed during chelate formation, resulting in a semi-quinone structure. As a result of the capping effect of bioactive compounds, Co(II) is reduced to a single Co atom, resulting in nano-sized particles.

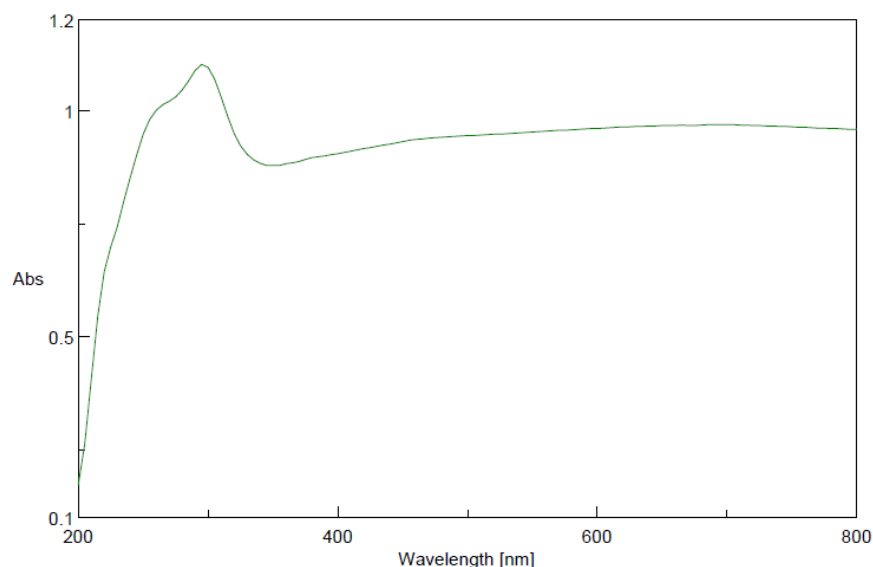


Fig. 4. UVDRS spectrum of Co₃O₄ NPs

3.5. Vibrational properties

The surface chemistry of the Co₃O₄ NPs was investigated using FTIR spectroscopy. Figure 5 shows the FTIR spectrum, which shows that many functional groups are involved in the creation of Co₃O₄ NPs. In the FTIR spectrum, there are six distinct absorption peaks at 3030, 2329, 1510, 1382, 1033, 656, and 559 cm⁻¹. The extensive absorption peak at 3030 cm⁻¹ is due to hydroxyl group OH-stretching or the presence of free OH groups. The bio-synthesis of Co₃O₄ NPs from the biological reduction of cell-free *Polyalthia longifolia* extract was suggested by the characteristic absorption bands of various functional groups (i.e., phenols, acids, protein, and polypeptides). Additionally, negatively charged carboxylate groups of free cysteine residues and free amine groups are used to record polypeptide and protein binding to NPs. Polypeptides and proteins, which are the most bioactive molecules in the *Polyalthia longifolia* extract, were found to be responsible for the reduction and stabilization of Co₃O₄ NPs.

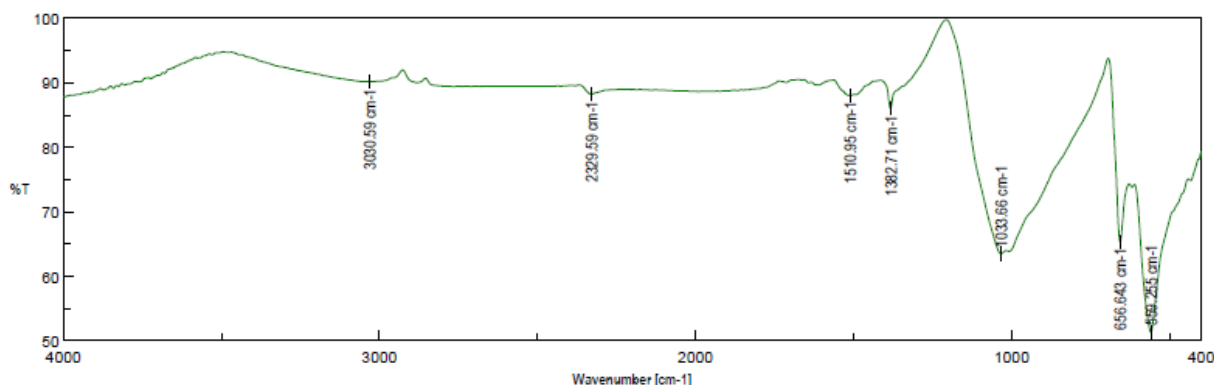


Fig. 5. FTIR Spectrum of Co₃O₄ NPs

3.6. Photoluminescence study

The PL spectroscopy method is a powerful tool for detecting blotches in semiconductors. Co₃O₄ NPs emit a high existence-related UV emission at 290 nm, as shown in Fig. 6. With the increase of annealing temperatures, grain limits and the number of grains on the surface of the nanostructure decrease as UV emission grows in

tandem with grain size and crystal orientation reduction. As a result, the amount of non-radioactive decay and crystal blotches suppresses each other, raising the amplitude of UV emission. The progression of the NPs' crystalline nature can be seen in this action. As a result, the absorption spectrum obtained has a blue change.

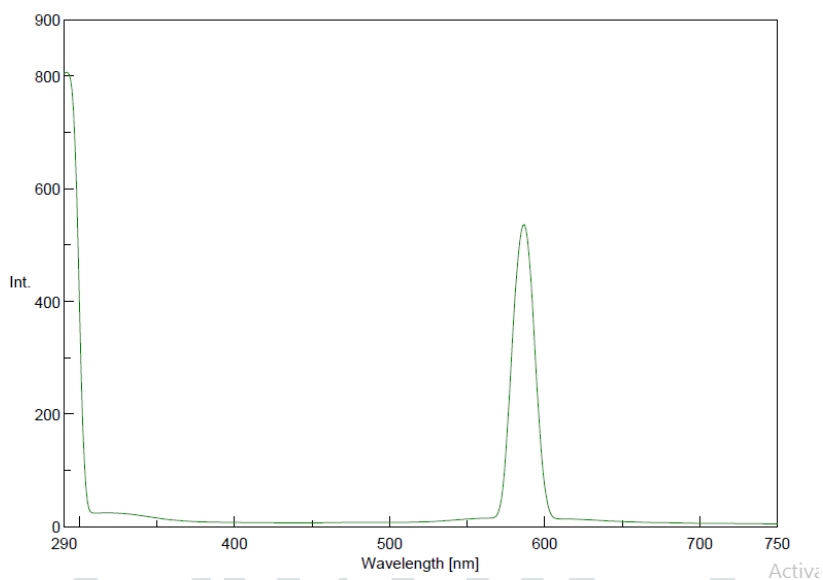


Fig. 6. PL spectrum of Co_3O_4 NPs

4. Conclusion

The natural extract of *Polyalthia longifolia* was used as an efficient bio-reduction/bio-oxidizing chemical agent in the green synthesis of high-purity amorphous Co_3O_4 quasi-spherical NPs. Thermal annealing at 400°C for 2 hours under standard air conditions results in crystallized single-phase Co_3O_4 NPs, as shown by SEM, EDX, XRD, FTIR, UV-DRS, and PL analyses. The next step will be to figure out what causes the Co_3O_4 NPs to form during the interaction between the Cobalt precursor and the *Polyalthia longifolia* leaves extract, as well as to track the dynamic of Co_3O_4 NPs formation.

References

1. Askarinejad A, Bagherzadeh M, Morsali A. Catalytic performance of Mn_3O_4 and Co_3O_4 nanocrystals prepared by sonochemical method in epoxidation of styrene and cyclooctene. *Applied surface science*. 2010 Sep 1;256(22):6678-82.
2. Shinde VR, Mahadik SB, Gujar TP, Lokhande CD. Supercapacitive cobalt oxide (Co_3O_4) thin films by spray pyrolysis. *Applied Surface Science*. 2006 Aug 15;252(20):7487-92.
3. Li WY, Xu LN, Chen J. Co_3O_4 nanomaterials in lithium-ion batteries and gas sensors. *Advanced Functional Materials*. 2005 May;15(5):851-7.
4. Jodłowski PJ, Jędrzejczyk RJ, Rogulska A, Wach A, Kuśtrowski P, Sitarz M, Łojewski T, Kołodziej A, Łojewska J. Corrigendum to “Spectroscopic characterization of Co_3O_4 catalyst doped with CeO_2 and PdO for methane catalytic combustion” [*Spectrochim. Acta A: Mol. Biomol. Spectrosc.* 131 (2014) 696–701]. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*. 2015(147):334.

5. Kaviyarasu K, Raja A, Devarajan PA. Structural elucidation and spectral characterizations of Co₃O₄ nanoflakes. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*. 2013 Oct 1;114:586-91.
6. Salavati-Niasari M, Mir N, Davar F. Synthesis and characterization of Co₃O₄ nanorods by thermal decomposition of cobalt oxalate. *Journal of Physics and Chemistry of Solids*. 2009 May 1;70(5):847-52.
7. Li X, Zhang Z, Tao L, Gao M. Sensitive and selective chemiluminescence assay for hydrogen peroxide in exhaled breath condensate using nanoparticle-based catalysis. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*. 2013 Apr 15;107:311-6.
8. Thota S, Kumar A, Kumar J. Optical, electrical and magnetic properties of Co₃O₄ nanocrystallites obtained by thermal decomposition of sol-gel derived oxalates. *Materials Science and Engineering: B*. 2009 Aug 15;164(1):30-7.
9. Dong C, Xiao X, Chen G, Guan H, Wang Y. Hydrothermal synthesis of Co₃O₄ nanorods on nickel foil. *Materials Letters*. 2014 May 15;123:187-90.
10. Zhang P, Hu GX, Bao SJ, Guo J, Lei C, Cai CJ, Jia DZ, Wang RY. One step microwave synthesis and magnetic properties of Co₃O₄ octahedrons. *Materials Letters*. 2012 Sep 15;83:195-7.
11. Makhlof MT, Abu-Zied BM, Mansoure TH. Effect of calcination temperature on the H₂O₂ decomposition activity of nano-crystalline Co₃O₄ prepared by combustion method. *Applied Surface Science*. 2013 Jun 1;274:45-52.
12. Li H, Fei GT, Fang M, Cui P, Guo X, Yan P, De Zhang L. Synthesis of urchin-like Co₃O₄ hierarchical micro/nanostructures and their photocatalytic activity. *Applied surface science*. 2011 May 15;257(15):6527-30.
13. Dai G, Liu S, Liang Y, Luo T. Synthesis and enhanced photoelectrocatalytic activity of p-n junction Co₃O₄/TiO₂ nanotube arrays. *Applied Surface Science*. 2013 Jan 1;264:157-61.
14. Sinha T, Ahmaruzzaman M. A novel and greener approach for shape controlled synthesis of gold and gold-silver core shell nanostructure and their application in optical coatings. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*. 2015 Jun 15;145:280-8.
15. Pourmortazavi SM, Taghdiri M, Makari V, Rahimi-Nasrabadi M. Procedure optimization for green synthesis of silver nanoparticles by aqueous extract of *Eucalyptus oleosa*. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*. 2015 Feb 5;136:1249-54.
16. Malleshappa J, Nagabhushana H, Kavyashree D, Prashantha SC, Sharma SC, Premkumar HB, Shivakumara C. Shape tailored green synthesis of CeO₂: Ho³⁺ nanopowders, its structural, photoluminescence and gamma radiation sensing properties. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*. 2015 Jun 15;145:63-75.
17. Sivakumar S, Venkatesan A, Soundhirarajan P, Khatiwada CP. Synthesis, characterizations and anti-bacterial activities of pure and Ag doped CdO nanoparticles by chemical precipitation method. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*. 2015 Feb 5;136:1751-9.

18. Pansambal S, Deshmukh K, Savale A, Ghotekar S, Pardeshi O, Jain G, Aher Y, Pore D. Phytosynthesis and biological activities of fluorescent CuO nanoparticles using *Acanthospermum hispidum* L. extract. *Journal of Nanostructures*. 2017 Jul 1;7(3):165-74.
19. Savale A, Ghotekar S, Pansambal S, Pardeshi O. Green synthesis of fluorescent CdO nanoparticles using *Leucaena leucocephala* L. extract and their biological activities. *J. Bacteriol. Mycol. Open Access*. 2017;5(5):00148.

