Biofabrication of CuO nanoparticles from *Cicer arietinum* pod extract and characterization

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Abstract

The use of the various plant waste parts for the synthesis of metal and metal-oxide nanoparticles is an eco-friendly and cost-effective protocol. The natural plant extract are non-toxic, biodegradable and act as reducing agent for the synthesis of metal and metal-oxide nanoparticles. The present research reports the fabrication of Copper oxide nanoparticles (CuO NPs) using pod extract of Cicer arietinum (Green Chickpea). The polyphenols present in methanolic extract of Chickpea pod act as capping agent, reducing agent and stabilizing agent for the synthesis of CuO nanoparticles. The CuO NPs results from Cupric acetate as a precursor followed by sonication, centrifugation and calcination. The resultant CuO NPs are then characterized by UV- spectroscopy, Fourier Transform Infrared Spectroscopy (FTIR), X-ray Diffraction (XRD), and Scanning Electron Microscopy (SEM). The synthesized CuO nanoparticles have cubic lattice structure with average crystalline size calculated from Scherrer formula found 10-15nm. This synthesized CuO NPs will be more efficient in catalytic reactions, photochemical reactions and environmental remediation.

Keywords: biofabrication, copper-oxide nanoparticles, Cicer arietinum, green chickpea, phytochemical.

INTRODUCTION

Nanotechnology has received extensive attention as they show various enamour characteristic than that of its bulk material [1] that make its environmentally benevolent process. Metal and metal oxide nanoparticles synthesized by chemical means are highly toxic, uses organic solvent and harsh reducing agent [2-4]. However, enzyme, micro-organism and plants mediated green synthesis of nanoparticles attains greater attention as they are eco-friendly and non-toxic [5], [6]. Synthesis of metal and metal-oxide nanoparticles have attracted considerable interest owing to their diverse function such as in catalysis, biomedical sciences, sensors, fabrication of electronic and optoelectronic devices. Of the numerous metal oxide nanoparticles, CuO nanoparticles attracted attention because of its narrow band gap of 1.2 eV and high-temperature p-type semiconductors. Cupric oxide (CuO) nanoparticles have potential application in biosensor [7], dye-sensitized solar cells [8] and for the fabrication of effectual electronic and optoelectronic devices [9].

CuO NPs synthesized through sonochemical [10], sol-gel technique [11], precipitation-pyrolysis [12], electrochemical method [13], microwave irradiations [14] etc. chemical methods are highly toxic and reactive to the environment and therefore they are inconvenient. To overcome all these effectiveness, a green approach to synthesize the CuO NPs are more efficient, non-toxic, inexpensive and eco-friendly. Various plant-mediated synthesized of CuO NPs have been reported such as from *Calotropis gigantean* [15], *Carica papaya* [16], *Gloriosa superba* [17], *Aloe barbadensis Miller* [18], *Gundelia tournefortii* [19] and *Ixora coccinea* [20]. The literature survey unveils that there is no report exist on the biosynthesis of cupric oxide nanoparticles using the plant *Cicer arietinum*.

The genus *Cicer arietinum* belongs to the family Fabaceae, commonly known as Green Chick pea. The green chickpea pod are the rich sources of polyphenols such as hydroxycinnamic compounds, o-dihydric phenols, hydrophobic phenols and hydrophilic phenols [21]. Thus, the waste part of chickpea plant can be applied for the synthesis of CuO nanoparticles.

EXPERIMENTAL

Instrument and reagents. The chemicals Cupric acetate monohydrate, methanol, sodium hydroxide pellets were purchased from sd-fine limited. These chemicals were used without any further purification and double distilled deionized water was used. UV-Visible Spectrophotometer (Labtronics) Model LT-2900 was used to characterize the sample for UV spectral analysis. FTIR analysis were recorded from Bruker Alpha FTIR Spectrophotometer in the range of 4000cm^{-1} to 400cm^{-1}. PAN analytical XPERT-PRO X-ray diffractometer with Cu-Kα1 and Kα2 radiation of λ 1.540598 Å and 1.544426 Å respectively with 0.5 fixed divergence and NO as monochromator using voltage of 40kV with scanning 2θ range of 20˚ to 80˚ at 0.02˚ min^{-1} was done for X-ray diffraction analysis. SEM ZEISS-EVO-18 Special Edition instrument was used for analysis of Scanning Electron Microscopy (SEM) Image and Energy Dispersive X-ray (EDX) image.

Preparation of Cicer arietinum pod extract. Cicer arietinum (Green Chickpea) pod were collected in month of Jan-Feb. The pods were shed-dried and then ground to make a powdered form. 20 g of chickpea pod powder were added with methanol and distilled water of 4:1 ratio. Continuous stirring at 400rpm for 4hr. at 80˚C was done for making the chickpea pod extract. Now, the solution were filtered to obtain the clear solution of pod extract.

Synthesis of Cupric oxide Nanoparticles (CuO NPs). The known amount of cupric acetate monohydrate diluted with 10 ml of double distilled water. The reaction was setup under low temperature with continuous stirring at 550 rpm. Now, the chickpea pod extract solution were added dropwise prior to addition of sodium hydroxide solution and the reaction was carried out for 14-16 hr. After this, solution were sonicated for 15 min and then centrifuged at 8000 rpm two times with doubled distilled water. The resultant product were dried in hot air oven at 80 ˚C overnight and then calcined at 500 ˚C. The obtained product were mashed with mortar-pestle to get fine powder for characterization purposes.

RESULT AND DISCUSSION

The resultant powder and chickpea pod extract were characterized through various spectral analysis for synthesized CuO nanoparticles. UV spectrophotometer is used to analyse the synthesis of metal-oxide nanoparticles and plant constituent properties. The Figure 1 shows the

absorption at 266 nm for π-π* transition due to presence of polyphenols constituents in green chickpea pod. The capped CuO NPs shows the Surface Plasmon Resonance (SPR) at 270 nm.

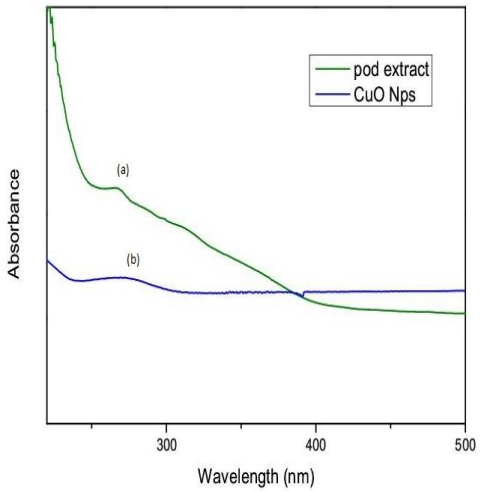

Figure 1. UV-Vis spectra of (a) Cicer arietinum (Green Chickpea) pod extract (b) synthesized CuO NPs

The FTIR spectra of Figure 2 shows the presence of functional groups that are responsible for the synthesis of CuO NPs. The FTIR spectra of chickpea pod extract shows the wide band at 3499 cm^{-1} for N-H group, 2950 cm^{-1} for O-H group and 2842 cm^{-1} for C-H group. The band at 2077 cm^{-1} corresponds for alkynes and nitriles group. The presence of C=O, C=C, C=N group shows the band at 1645 cm^{-1}, 1453 cm^{-1}, 1411 cm^{-1} and also confirms the presence of aromatic ring. The band at 1109 cm^{-1}, 1018 cm^{-1} are responsible for C-C, C-O, C-N bond. The weak band at 647-408 cm^{-1} contributes for bending vibrations. The band at 483-407 cm^{-1} corresponds to the presence of metal-oxygen bond.

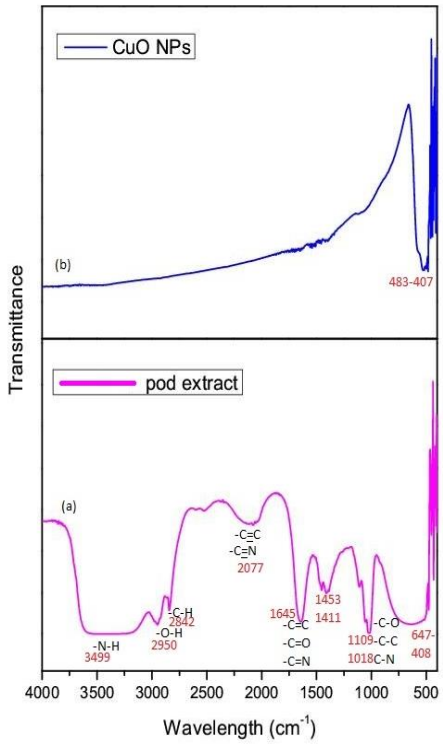

Figure 2. FTIR Spectrum of (a) Cicer arietinum pod (Green Chickpea) extract and (b) synthesized CuO Nps.

The XRD data from Figure 3 reveals the information about that the synthesized CuO NPs are nano-sized and crystalline in nature. All the XRD peaks were indexed by monoclinic phase of CuO (JCPDS Card No. 80-1916). The diffraction peaks were observed at 2θ values of 32.53˚, 35.51˚, 38.71˚, 48.89˚, 58.20˚, 61.54˚, 66.43˚, 68.22˚, 72.52˚, 75.27˚ corresponds for the lattice plane [110], [111], [200], [202], [020], [202], [113], [311], [220], [400], respectively. The average crystalline size of the prepared CuO nanoparticles were calculated by applying Debye- Scherer equation [22].

$D = K\lambda / \beta \cos\theta$

where, D is the crystalline size of the nanoparticles, K is Scherer's constant (0.89), λ is the wavelength of X-ray (1.54 Á) used in XRD, β is the full width at maxima (FWHM) of the high intensity diffraction peak and θ is the angle of Bragg's diffraction. At 2θ = 35.51˚; β = 1.226 (by Origin Pro 8.5), the D value found to be approximately 12.76 nm. Thus, the synthesized capped CuO NPs has the crystalline size in the range of 12.76 nm respectively.

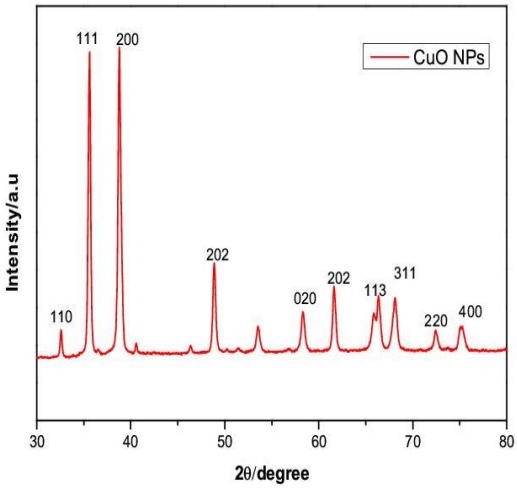

Figure 3. XRD analysis of synthesized CuO NPs.

Scanning Electron Microscopy (SEM) gives the information about the morphology and composition of the prepared samples. SEM images shows the particles are hexagonal shape and its composition were confirmed by EDX in Figure 4 and Figure 5. The EDX shows that the synthesized samples are CuO NPs with Copper (Cu) 68.05 % weight and Oxygen (O) 30.95 % weight respectively. The presence of Magnesium (Mg) and Silicon (Si) from the plant extract in the synthesized samples also reveals the information that the polyphenols present in Green Chickpea pod act as capping and stabilising agent for synthesis of CuO NPs.

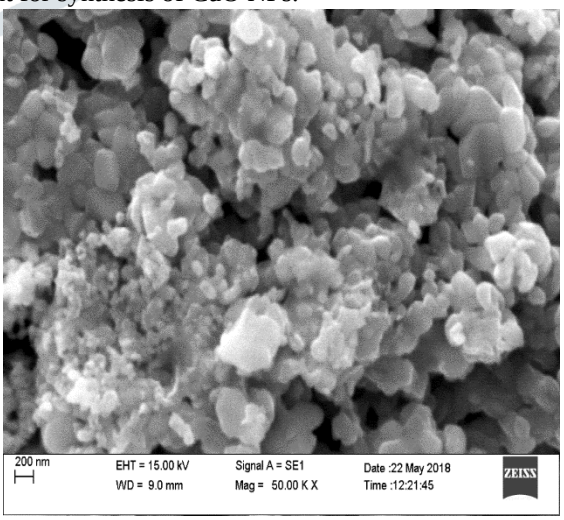

Figure 4. SEM image of synthesized capped CuO NPs.

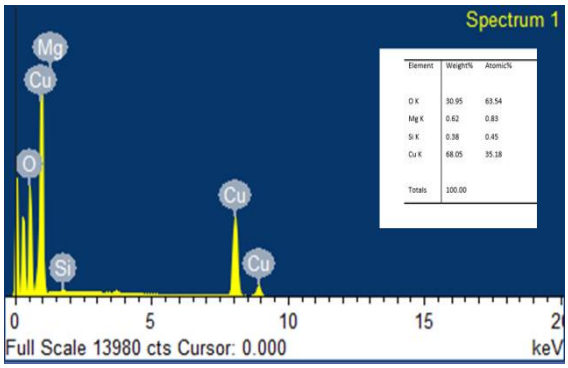

Figure 5. Energy Dispersive X-ray (EDX) image of synthesized CuO NPs.

CONCLUSION

The present research focussed on the biofabrication of CuO NPs from the Green Chickpea pod extract. The presence of polyphenols such as hydroxycinnamic compounds, o-dihydric phenols, hydrophobic phenols and hydrophilic phenols in chickpea pod extract serves as reducing, capping, and stabilising agent for synthesis of CuO nanoparticles. Here, the use of the biological waste for the synthesis of metal-oxide nanoparticles are shown with the best result. This green approach synthesized CuO NPs are most applicable for catalytic reaction, photochemical reaction, biomedical, and for biotechnology purposes.

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