Green synthesis of copper oxide nanoparticles using aqueous extract of flowers of *Cassia alata* and particles characterisation

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**Abstract**

Water-soluble cupric oxide nanoparticles are stable over a wide range of pH and temperature. This excellent stability in the form of aqueous colloidal suspensions makes the application of the water-soluble CuO nanoparticles easier in aqueous systems. In the present study, copper oxide nanoparticles are synthesized using flower extract (aqueous) of *cassia alata* L., a shrub, member belonging to family Fabaceae profusely growing in the wild. The synthesized nanoparticles are subjected to SEM, EDX, XRD to understand the particle characteristics of the copper oxide nanoparticles which closely matched with JCPDC standard.

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**Introduction**

Nanoparticles are considered as building blocks of the next generation of technology with applications in many industrial sectors. In particular, metal oxide nanoparticles are receiving increasing attention in a large variety of applications. Metal oxide nanoparticles are of interest because of their unique optical, electronic and magnetic properties. The oxides of transition metals are an important class of semiconductors, which have applications in magnetic storage media, solar energy transformation, electronics, gas sensors and catalysis (Guajardo-PachecoMa, 2010; Ahmad et al., 2011). Various physical and chemical methods have been extensively used to produce nanocrystalline copper oxide such as sonochemical (Kumar et al. 2000; Vijayakumar et al. 2001); hydrothermal (Zhang et al., 2006) and microwave radiation (Wang et al., 2004). sol–gel technique (Eliseev et al., 2010); one-step solid state reaction method at room temperature (Xu et al., 1999). Electrochemical method (Borogohain et al., 2000); thermal decomposition of precursors and co-impregnation of metal and oxygen ions (Nakao et al., 2002). Cu nanoparticles are synthesized from vapor deposition (Hyungsoo 2004, Gericke, 2006) electrochemical reduction (Huang et al., 2007) radiolysis reduction (Joshi et al., 1998) thermal decomposition (Aruldas et al., 1998), chemical reduction of copper metal salt (Hashemipour et al., 2011, Vijayakumar et al., 2001. Hung-Hsiao Lin, 2004 and Seung-Deok Seo et al., 2011). Further, biological methods for nanoparticle synthesis using plants for nanoparticle synthesis can have advantages over other biological processes because it eliminates the elaborate process of maintaining cell cultures and can also be suitably scaled up for large-scale nanoparticle synthesis. In the current context, importance is being given to the fabrication of a wide range of nanoparticles for developing environmentally benign technologies in materials synthesis (Bhattacharya and Rajinder, 2005). Among the oxides of transition metals, copper oxide nanoparticles are of special because of their efficiency as nanofluids in heat transfer application. For example it has been interest reported that 4 % addition of CuO improves the thermal conductivity of water by 20 % (Lee et al., 1999). Water-soluble cupric oxide nanoparticles are CuO nanoparticles are stable over a wide range of pH and temperature. This excellent stability in the form of aqueous colloidal suspensions makes the application of the water-soluble CuO nanoparticles easier in aqueous systems. Reports on biosynthesis and characterization of nanocrystalline CuO are relatively few and method for the synthesis of CuO nano-particles is simple, mild, and environmentally friendly. Therefore, in the present study, copper oxide nanoparticles are synthesized using flower extract (aqueous) of *cassia alata* L., a shrub, member belonging to family Fabaceae profusely growing in the wild.

**Materials and Methods**

Fresh flowers of healthy Cassia alata were collected from pondicherry university campus, India. *Cassia alata* L. or *senna* is a shrub, 2-3m high, widely distributed in the tropical countries. It is native to South America, but has been planted widely for medicinal and ornamental purposes.
and thus it has become as invasive plant. It is known as ringworm shrub, winged Senna, candle tree or ringworm Copper Sulphate salt, as a source of Copper was purchased from Himedia Laboratories Pvt. Ltd., Mumbai, India. **Preparation of flower extract (aqueous) and 1.0mM Copper sulphate solution.**

The plant extract has been prepared by the method described by Aboud et al (2013). Aquous extract of flowers of *Cassia alata* was prepared using freshly collected flowers. They were cleaned in running tap water, followed by distilled water and then the flower are cut into small pieces, crushed with the help of morter and pestle, the fine colloidal extract was filtered through muslin cloth and the filtrate was collected and diluted with distilled water(100ml). This solution is used for synthesis. 0.169gm of copper sulphate salt in 1000 ml of distilled water to get 1.0mM solution of copper sulphate and stored. 50ml of plant extract and 50ml of CuSO4 solution was taken in two separate beakers and heated at 60˚c for 30 min in water bath.

**Green synthesis of copper oxide nanoparticles**

For the synthesis of copper oxide nanoparticles, heated 1.0 mM CuSO4 solution was added to the heated plant extract at 1:1 ratio and stirrer with glass rod for 10min and heated in heating mantle for 45min at 80˚c. CuO nanoparticles synthesis is indicated by turning of light brown colour to pale green. The change in the colour of the reactants indicates the formation of copper oxide nanoparticle. The content was washed in double distilled water thrice by repeated centrifugation at 5000 rpm 15 min and the sediments was collected and stored for further characterization after drying in an oven at 110˚c over-night. Oven-dried particles are characterized thro EDS, SEM, and XRD to get details on particles/crystals.

**Analysis of copper oxide nanoparticles**

For UV-visible spectrophotometer (Varian Model) analysis, 0.1ml of the sample is taken in a cuvette and was diluted to 2ml with deionizer water and the UV-visible spectra is obtained. From XRD spectrum, the prepared particles in solution was purified by repeated centrifugation at 5000 rpm for 20 min. For XRD (Rigaku ultima IV) analysis the pellets of copper nanoparticles were redispersed into 10ml of deionized water. Then freeze dry the purified particles. The dried mixture of copper nanoparticles was collected for the determination of the formation of Ag nanoparticles by X’pert pro x-ray diffractometer operated at a voltage of 40 KV and a current of 30 ma with Cu Kα radiation in 0–2 θ configuration. Further, to get information on the topography of the particles, aqueous suspension of copper nanoparticles were fabricated by dropping the suspension onto clean electric stubs and allowing water to completely evaporate. SEM observation were carried out on a Hitachi, Model: s-3400n Electron microscope (CIF Pondicherry University) and ZEISS EVO 40 EP Electron microscope. Further, To obtain elemental details on the nano suspension, it is subjected to EDX analysis. EDX identifies the elemental composition of materials imaged in a scanning Electron Microscope (SEM) for all elements with an atomic number greater than boron. Most elements are detected at concentration on the order of 0.1%. as the electron beam of the SEM is scanned across the sample surface: it generates X-ray fluorescence from the atom in its path. The energy of each X-ray photon is characteristic of the element which produced it. The microanalysis system collected the X-rays, sorts them by energy, and automatically identifies and labels the elements responsible for the peaks in this energy distribution.

**Results**

During the biosynthesis, formation of nanoparticles is indicated by the change in colour of the mixture (copper sulphate and flower extract) from dark brown to pale green after 2 hours of reaction (Fig. 2). The filtered, washed and dried particles obtained from reaction mixture, showed a broad peak at 263 nm in the UV-Vis spectrophotometer indicating the presence of copper oxide (Fig.3). EDX spectrum showed the presence of elemental copper along with minor impurities (Fig.4). XRD values of 2θ showed peaks at 32˚, 23˚, 33.21˚, 35.59, 38.60, 46.22, 54.93, 57.93 which are comparable to JCPD Standards (Fig5). With Energy Dispersive X-ray Spectroscope (EDX) analysis, the presence of elemental copper oxide signal was confirmed in the sample. The presence of impurities are attributed to the extracellular organic element is adsorbed on the surface of the metallic nanoparticles. The appearance of silica and aluminium in the EDX spectrum is because of the aluminium grid base and silica holder used during spectral sample preparation and these are considered as preparation borne impurities.
Fig. 3  UV-visible absorption spectrum

Fig. 4  XRD spectrum of synthesized copper oxide

Fig. 5  EDX showing elemental copper synthesised
Table. Elemental composition from EDX
Live Time: 15.0 sec.

<table>
<thead>
<tr>
<th>Element</th>
<th>Net Counts</th>
<th>Net Counts Error</th>
<th>Weight %</th>
<th>Atom %</th>
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<tr>
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<td>61.70</td>
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<tr>
<td>O K</td>
<td>969</td>
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<td>32.61</td>
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<tr>
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<tr>
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<tr>
<td>P K</td>
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<tr>
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<td>+/- 36</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
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<td></td>
<td></td>
<td>100.00</td>
<td>100.00</td>
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</table>

Fig.6 SEM images of synthesized copper oxide nanoparticles

The scanning electron microscopic (SEM) was done using Hitachi model s-3400n SEM machine. The magnification was done at 20um, 10um and 5um. From the image we conclude that the nanoparticles are clustered. The surfaces of the aggregates are rough. The particles are more or less spherical and range from 110-280nm in size.

Discussion

Biological synthesis of nanoparticles using microorganisms, enzymes, and plant part extracts has been the subject matter of researchers in the recent past as an eco-friendly alternative to a variety of chemicals involve synthetic/chemical methods. Using plants as bio reductants can have advantages over other biological processes like using microbial population because it eliminate elaborate process of maintaining cell culture and can be suitable scaled up for large-scale synthesis. In this pursuit, presently aqueous extract of flower of Cassia alata belonging to family Fabaceae, was used as reactant to nucleate nanoparticles in solution. The formation of CuO nanoparticles was confirmed primarily based on change in color of the reaction mixture after 2hrs at room temperature and also by UV spectrum which is frequently used to characterise synthesized metal oxide nanoparticles. The change in colour of reaction mixture is due to surface plasmon resonance phenomenon which provides a convenient indication of formation of copper oxide nanoparticles. The synthesized copper oxide particles are subjected to UV- spectroscopic analysis and obtained a single beak but broad at 263nm indicating the presence of oxide of copper metal. Similar observation was also made by (Ahmed et al, 2003)

Further, the synthesized particles are subjected to which has given a clear picture on the presence crystalline cubic phase of monoclinic Cupric oxide(CuO) exhibiting 20 values 32˚,23˚, 33.21˚, 35.59, 38.60, 46.22, 54.93,57.93 which are closely matched with the values of monoclinic phase CuO reported by Volante et al (2008). Vinod et al (2013), Amrut et al (2010) and recently by Abboud et al (2013). Above all, it is encouraging to note that the 20 values of the synthesized copper oxide nanoparticles are also matched with Joint Committee for Powder Diffraction Standard (JCPDS). The SEM images indicated that the crystalline CuO are cuboid and size of particles is ascertained from the SEM scale ranged between 110-280nm.

To find out the purity of the metal particles synthesized, EDX spectrum was obtained which showed along with copper, there were other elements viz. Al and Si. It was attributed by the aluminium grid and silica holder used in the process of sample preparation. Thus, the aqueous extract of flowers of a wild plant Cassia alata is found to be a potential source bio-reductant to reduce metal salts into their nanoparticles. However, with regard to the chemical reaction involved in the biosynthesis of CuO...
nanoparticles between copper sulphate and flower extract, so for none of the biochemical constituents, has been reported as the causative factor for synthesis. But based on the phyto-chemical constituents of plants that are used as bio-reductance so far, it has been attributed that phyto-chemical constituents like carboxylic groups and amino acids (Beveridge and Murray, 1980), deterpenoids (Ahmed et al. 2013), enzymes (Mandal et al, 2006) and abundance of hydroxyl and carboxylate groups present in plants might have facilitated the formation of Cu (OH)2, which hydrolyzed later into nanocrystalline CuO. (Vinod Vellora et al. 2013). None the less, it is presumed that the phytochemical constituents either individually as synergetically could have influenced the bio-reduction in such metal oxide nanoparticles synthesis. Further intensive screening of flowers for phyto-chemical constituents, would unveil the underlying chemical reaction & kinetics for its small scale production of CuO nanoparticles and wider application in environmental management, biotechnology and medicine.

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References


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