Research Article

Aqueous Extract of *Saraca indica* Leaves in the Synthesis of Copper Oxide Nanoparticles: Finding a Way towards Going Green

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The present study is mainly aimed at the synthesis of copper oxide nanoparticles of varied size by green synthetic approach. The structural and morphological behavior of as-synthesized CuO nanoparticles were investigated using ultraviolet-visible spectral studies (UV-Vis), Fourier transform-Infrared spectroscopy (FT-IR), X-ray diffraction (XRD), energy dispersive X-ray spectroscopy (EDX), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and high-resolution transmission electron microscopy (HRTEM). The reduction of copper ions using aqueous extract of *S. indica* leaves produces nanoparticles of varied size and morphology. The images from SEM investigation revealed that the particles are spherical in shape with average diameter of 40–70 nm. TEM and HRTEM images clearly indicate the crystallinity and spherical nature of as-synthesized CuO nanoparticles with interplanar distance between two neighboring lattice fringes of 0.315 nm.

1. Introduction

Cupric oxide (CuO) nanoarchitectures are of special interest because of their interesting properties and promising applications in batteries, solar cells, gas-sensors, biosensors, catalysis, photodetectors, and removal of toxic pollutants from waste water [1]. Due to some toxic chemicals absorbed on the surface of nanoparticles when they are prepared by conventional chemical methods and that may cause adverse effects in medical applications, researchers are constantly making enormous findings in synthesizing nanoparticles by green approach. Very recently, eco-friendly synthesis of various nanoparticles by plants such as neem [2], alfalfa [3, 4], *Cinnamomum camphora* [5], *Embllica officinalis* [6], lemon grass [7], and tamarind [8] have been reported. *Saraca indica*, commonly known as Ashoka tree, is generally found in the Western Ghats of Indian subcontinent. Till date, the use of extract from this plant is limited and thus we approached

synthesizing CuO NPs using aqueous extract of leaves of Ashoka tree.

Herein, we describe the synthesis of CuO nanoparticles by reducing copper ions using natural reducing agent, *Saraca indica* leaf extract. In addition, the used plant extract also served as capping agent in stabilizing the as-synthesized CuO NPs. The varied size and morphology of the obtained nanostructures were characterized using FT-IR, UV-Vis, XRD, EDX, XPS, SEM, TEM, HRTEM, and SAED techniques. In addition, the photoluminescence behavior of CuO NPs under study was described.

2. Experimental

2.1. Materials and Methods. Starting material, hydrated copper chloride [CuCl₂·H₂O] procured from Sigma (USA), and acetone were obtained from Merck chemical suppliers, India. Deionized water collected from ELGA purifier was used

throughout the experimentation. The electronic absorption spectra were obtained using Perkin Elmer Lambda 750 UV-Visible spectrometer. The fluorescence studies were performed on Horiba JOBIN YVON Fluoromax-4 spectrometer. FT-IR spectra were obtained on IR spectrometer (Shimadzu). Powder XRD was recorded on Bruker X-ray diffractometer using a $\text{Cu K}\alpha$ ($1.5406 \text{ \AA}$) radiation. X-ray photoelectron spectroscopy (XPS) was recorded using a MULTILAB 2000, Thermo Scientific, UK. Energy dispersive spectra (EDS) was recorded using HITACH S-2400 energy dispersive X-ray spectrometer. Scanning electron microscopy (SEM) images and X-ray mapping were recorded on Zeiss microscope. Transmission electron microscopy (TEM) images and SAED pattern were recorded on JEOL 2100F FEG operating at 200 kV after casting a drop of CuO NPs dispersion in ethanol over Cu grid.

2.2. Plant Material Collection and Extraction. *S. indica* was collected from Udupi, Karnataka, India, during July to August 2016. The plant identification was explicitly performed by Dr. K. Shiva Prasad. The leaves were thoroughly washed and dried at room temperature for about 10 days and ground into a fine powder. The dried leaves (23.5 g) were extracted with water as a solvent by a soxhlet apparatus at 60°C (1:4 w/v). The obtained filtrate was reduced under rotary vacuum evaporator (Buchi) resulting in 7.8% of aqueous extract of *S. indica* leaves.

2.3. Synthesis of CuO Nanoparticles. To an aqueous solution of $\text{CuCl}_2 \cdot \text{H}_2\text{O}$ (1.34 g in 25 mL), *S. indica* leaf extract was added (0.29 g dissolved in 20 mL deionized water) and stirred for 1 h. The formation of ruby red colored solution from the above reaction mixture implies the formation of CuO NPs. The stirring was continued for another 2 h to obtain dark brown colored solution suggesting the formation of stabilized copper oxide nanoparticles. It was then filtered and washed with water followed by acetone and dried at 100°C for 6 h.

3. Result and Discussions

3.1. UV-Visible Absorption Spectra. Light absorption by a material leads to transmission of an electron into the conduction band and formation of a positive hole in the valence band. The UV-Visible absorption spectral studies of as-synthesized copper oxide nanoparticles were performed in a homogeneously suspended ethanol solution and are depicted in Figure 1. A strong absorption peak observed at around 213 nm was because of direct transition of electrons [9] and another absorption peak observed at 339 nm indicates the presence of optical band gap in CuO NPs (concentration is 0.1341 mg/mL). This kind of optical absorption permits us to determine the crystallinity of material upon comparison of their band gaps. These observations are consistent with the previously reported studies [10, 11].

3.2. FT-IR Spectroscopy. Figure 2 shows infrared spectra of obtained CuO NPs. A broadband at 3422 cm^{-1} is attributed to intermolecular hydrogen bonding between hydroxyl groups

FIGURE 1: UV-visible spectra of CuO NPs synthesized using aqueous extract of *S. indica* leaves.

of benzene ring containing acids and/or alcohol compounds [12]. The band observed at 1635 cm^{-1} is due to $\text{C}=\text{O}$ stretching of ketones and/or acids [13] present in the residual plant material. A narrow band was noticed at 575 cm^{-1} confirming the formation of pure CuO NPs.

3.3. XRD Measurements. As depicted in Figure 3, XRD patterns of as-synthesized CuO NPs are typical and are similar to the single phase monoclinic structure with a lattice constant $a = 4.6961 \text{ \AA}$ and $b = 3.4320 \text{ \AA}$ and $c = 5.1330 \text{ \AA}$ and $\beta = 99.5284^\circ$. The distinctive peaks located at $2\theta = 32.94^\circ, 35.83^\circ, 39.62^\circ, 59.02^\circ, 60.71^\circ$, and 64.89° are assigned to (110), (002), (200), ($\bar{2}02$), and (202) plane orientation of CuO (JCPDS 80-1268). It clearly revealed that nanosized CuO was successfully synthesized under current mild experimental conditions.

3.4. XPS Studies. Figure 4 shows XPS spectra of as-synthesized CuO NPs. The peaks centred at 939.87 eV and 954.57 eV corresponded to the Cu $2p_{3/2}$ and Cu $2p_{1/2}$, respectively. The higher binding energy of Cu $2p_{3/2}$ at 939.87 eV and the presence of shake-up peak at about 945–950 eV were two major XPS characteristics of CuO, indicating the existence of Cu^{2+} [14, 15].

3.5. EDX Investigations. The purity of the as-synthesized CuO NPs was investigated by EDX spectral measurements. The EDX spectra shown in Figure 5 reveals that the sample contains Cu, O, and Si. The presence of Si was due to the sample holder which might have appeared during sample preparation. This clearly indicates that the sample under investigation is free from impurity. Thus, the aqueous extract of leaves of *S. indica* is found to be a powerful eco-friendly reductant for reducing metal salts into their nanostructures.

3.6. SEM Analysis. The morphologies of as-synthesized CuO NPs are analyzed by SEM measurements, illustrated in

FIGURE 2: Infrared spectrum of prepared CuO NPs.

FIGURE 3: X-ray diffraction pattern of CuO NPs synthesized using aqueous extract of *Saraca indica* leaves.

FIGURE 4: XPS spectra of as-synthesized CuO nanoparticles.

Figure 6. From the SEM images, it can be clearly seen that as-synthesized CuO NPs mainly comprised of spherical agglomerates. The diameter of well-defined and fully developed agglomerate of as-synthesized CuO NPs varies between 40 and 70 nm.

3.7. TEM Investigations. Figure 7 depicts typical TEM images of as-synthesized CuO nanoparticles. The TEM image (Figure 7(a)) reveals that the product comprises spherical particles with a uniform morphology and size distribution with particle size in the range of 13–15 nm. High-resolution TEM (HRTEM) image of as-synthesized CuO nanoparticles is shown in Figure 7(b). The crystalline nature of the nanoparticles is clearly seen from the images shown in lattice fringes

FIGURE 5: EDX results obtained for CuO NPs under study.

FIGURE 6: SEM images of as-prepared copper oxide nanoparticles.

FIGURE 7: TEM images showing (a) spherical nature of as-synthesized CuO nanoparticles and (b) HRTEM image of CuO NPs and SAED pattern (inset image).

FIGURE 8: Fluorescence emission spectra of as-synthesized CuO nanoparticles in ethanol medium.

and the interplanar distance between two neighboring fringes is about 0.315 nm. The SAED pattern (inset in Figure 7(b)) reveals the single-crystalline nature of the CuO nanospheres. The size of the particles observed from TEM and HRTEM investigations is in good agreement with XRD diffraction pattern, confirming good crystallinity of the CuO nanospheres.

3.8. Photoluminescence Studies. The dispersed ethanolic solution of as-synthesized CuO NPs was used for photoluminescence measurements at room temperature. The broad emission maximum observed at 545 nm ($\lambda_{\text{ex}} = 350$ nm) in Figure 8 corresponds to band edge emission in CuO NPs which coincides well with the previous reports [16, 17]. The relatively low fluorescence emission maxima observed may be due to the luminescence arising from the recombination of excitons and/or shallowly trapped electron-hole pairs [18]. Thus, it clearly indicates that particles are fluorescent but not intensely fluorescent.

4. Conclusions

Facile synthesis of CuO NPs using *S. indica* leaf extract has been demonstrated. The self-accumulated nanospheres of copper oxide nanoparticles were prepared by using naturally occurring plant, *Saraca indica* (aqueous extract) as reducing and stabilizing agent. The 3D nanospheres have an average diameter of about 13–15 nm. The formation of CuO NPs was primarily noticed by observing color change during their synthesis and also by encountering a characteristic IR band at 575 cm^{-1} , attributed for Cu-O stretching vibrations. The morphology and crystal structure investigations by SEM, TEM, and HRTEM revealed the spherical nature of as-prepared CuO NPs with interplanar spacing 0.315 nm in the single crystal of CuO. The fluorescence emission intensity observed at 518 nm in the reported CuO NPs was due to recombination of excitons and/or shallowly trapped electron-hole pairs. Thus,

these could find interesting applications in fluorescence-emitting materials.

Competing Interests

The authors declare that they have no conflict of interests in the publishing of this research work.

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