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Black Tea Extract Mediated Green Synthesis of Copper Oxide Nanoparticles

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Abstract

Copper oxide nanoparticles were synthesized using black tea extract and copper nitrate as the copper source by the green method at different calcination temperatures. This method has many advantages such as nontoxic, economic viability, ease to scale up, less time consuming and environmental friendly approach for the synthesis of CuO nanoparticles without using any organic chemicals. The synthesized CuO nanoparticles were characterized by powder X-ray diffraction (XRD), scanning electron microscopy (SEM) and Fourier Transform Infrared Spectroscopy (FTIR). The average crystallite size of CuO nanoparticles was calculated using Scherrer formula. The X-ray powder diffraction (XRD) analysis revealed the formation of monoclinic phase CuO with average particle size of 22-39 nm.

Keywords: *CuO, Biosynthesis, Nanoparticles, Green method.*

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Introduction

Unlike bulk materials, nanoparticles have been intensively studied over the last decade due to their characteristics: physical, chemical, electronic, electrical, mechanical, magnetic, thermal, dielectric, optical and biological properties [1-3]. Therefore, 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 [4-8]. Copper Oxide is a p-type semiconductor with direct band gap and high absorption properties that make it a promising material for low-cost photovoltaic cells. Copper oxide nanoparticles are used in a wide range of applications such as gas sensors, magnetic storage media, solar energy transformation, semiconductors, and organic catalysis [9, 10]. For synthesis copper oxide nanoparticles, many efficient approaches have been carried out such as Sonochemical preparation [11], alkoxidebased preparation [12], microwave irradiation [13], precipitation-pyrolysis [14], and thermal decomposition [15]. Recently, green synthesis of CuO-NPs by plants such as *aloe vera* leaf extract [16], *Gloriosa superba* L. extract [17], *Coffee powder* extract [18] and *Cassia alata* [19] have been reported, As well as synthesis of various nanoparticles by black tea such as gold NPs [20], silver NPs [20, 21], palladium NPs [22], iron NPs [23] and gold-silver alloy NPs [24] have been reported.

In this work, we have synthesized copper oxide nanoparticles using black tea powder extract and water as solvent by green method, a cheap and friendly approach to the nature. The obtained samples were characterized by Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and X-ray diffraction pattern (XRD).

Experimental

Material and methods

Black tea powder was obtained at a local health food store. Copper nitrate trihydrate $Cu(NO_3)_2.3H_2O$ was purchased from daijung (Darmstadt, Korea) and used without further purification. The IR spectra were measured on a Jasco 6300 FT-IR spectrometer (KBr disks). The structural properties of synthesized nanoparticles were investigated by X-ray powder diffraction (XRD) pattern on a X'Pert-PRO advanced diffractometer using Cu (Kα) radiation (wavelength: 1.5406 Å) at 40 kV and 40 mA at room temperature in the range of 2θ from 20 to 80º. The particle size and morphology of the sample surfaces was studied by a scanning electron microscopy (LEO Co., England, Model: 1455VP). The sample disc was coated with gold in an ionization chamber.

Preparation of tea powder extract

To prepare the tea extract, 2 g of tea powder was dissolved in 100 ml of water and boiled for around 30 min. After cooling at room temperature, these were centrifuged for 20 min and filtered. The filtrates were stored at 5-10 ºC for further experiments.

Synthesis of CuO nanoparticles using tea extract

To prepare CuO-NPs, 2g of $Cu(NO_3)_2.3H_2O$ was dissolved in 10 ml of distilled water and then stirred for 5 min. After that, 30 ml of tea powder extract was added to the copper nitrate solution and the container was moved to a Sand bath. The temperature of the Sand bath was fixed at 75 ºC. Stirring was continued for 12 h to obtain a green color powder. The final product was calcined at different temperatures (500, 600, 700 and 800 ºC) in air for 4h to obtain CuO-NPs.

Results and discussion

Characterization of CuO nanoparticles.

FTIR spectra were recorded in solid phase using the KBr pellet technique in the range of 400-4000 cm^{-1}. Figure 1 shows the IR spectrum of the sample calcined at 600°C for 4 hours. The spectra show the stretching vibration mode for the CuO compound is seen at 533.35 cm^{-1} band. Two distinct bands are seen at 1053 cm^{-1} and 1651 cm^{-1} are attributed to the bending vibration of absorbed water molecule and surface hydroxyl group (OH), respectively. A broad vibration band is seen at 3430 cm^{-1} due to the O–H stretching vibration of absorbed water molecule and surface hydroxyl group [25].

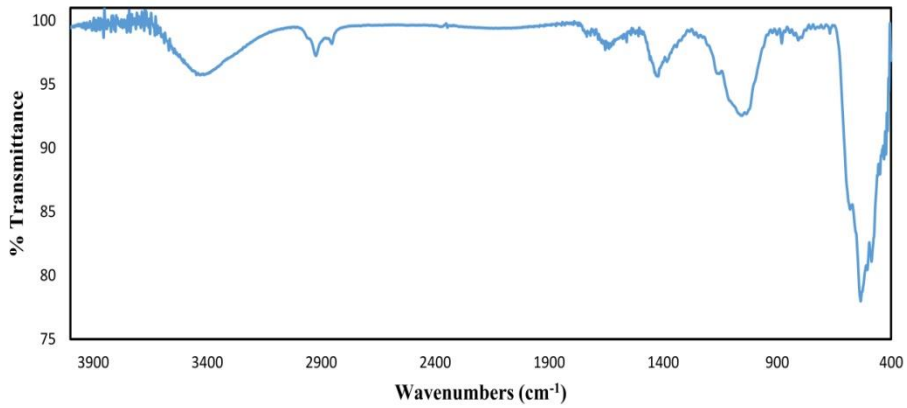


Figure 1. FT-IR spectrum of CuO NPs.

Figure 2 shows the XRD patterns of the sample after calcination at different temperatures. All the peaks of the patterns of the calcined samples at 500, 600, 700 and 800 correspond to pure CuO without any impurity phases.

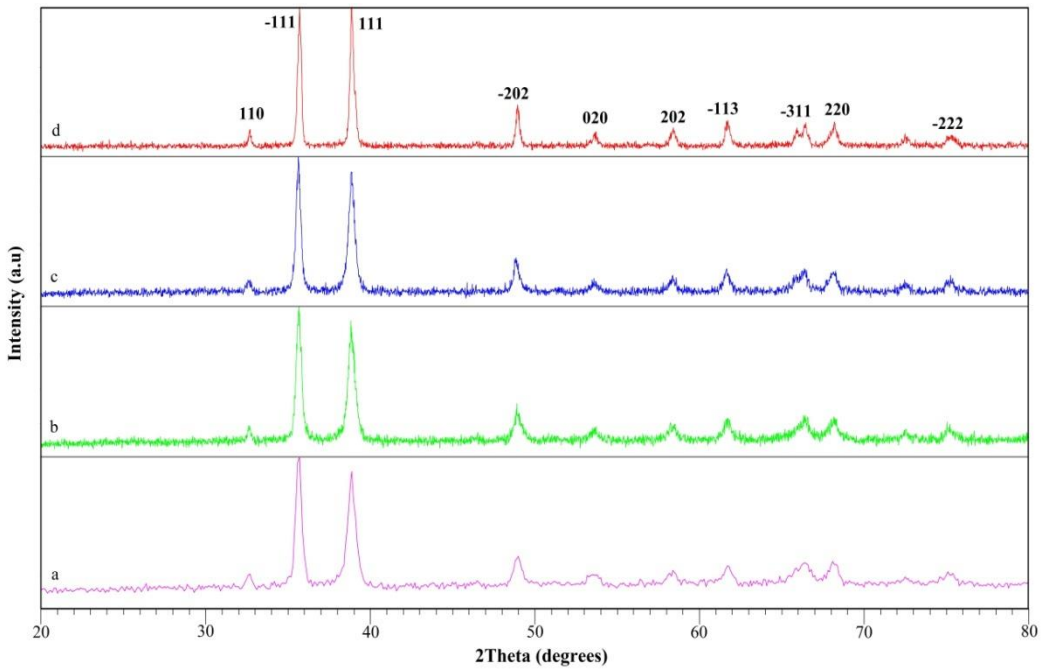


Figure 2. XRD patterns of synthesized CuO-NPs in air at different temperatures (a: 500; b: 600; c: 700 and d: 800 ºC).

XRD analysis showed a series of diffraction peaks at 2θ of 36.62, 35.63, 38.38, 48.81, 53.61, 58.36, 61.60, 66.35, 68.23 and 75.35 can be assigned to (110), (-111), (111), (-202), (020), (202), (-113), (-311), (220) and (-222) planes, respectively. All diffraction peaks were well matched with the monoclinic phase of CuO (standard JCPDS File No: 80-1268). The calculated lattice parameters for CuO NPs are a= 4.679 Å, b= 3.418 Å and c= 5.127 Å which are in good accordance with the standard XRD data (JCPDS file No. 80-1268). Furthermore, the strong and sharp diffraction peaks confirm the high crystallinity of the products.

The average particle size of CuO nanoparticles was determined from the full width at half maximum (FWHM) of the XRD patterns using the well- known Scherer formula:

$D = 0.9\lambda/\beta\cos\theta$

Where D is the crystallite size (nm), β is the full width at half maximum of the peak, λ is the X-ray wavelength of Cu Kα= 0.154 nm and θ is the Bragg angle [26]. Using the above method the variation of crystallite size with temperature was calculated and the results are presented in Table 1.

Table 1. Variation of crystallite size with annealing temperature.

Temperatures (°C)	Crystallite size (nm)
500	22.3
600	27.2
700	33.5
800	38.7

The SEM image shows the particle size and external morphology of the CuO nanoparticles that calcined at 600 ºC for 4h (Figure 3). It can be seen from the SEM image the cupric oxide nanoparticles have fairly uniform spherical shape and narrow size distributions. It shows that the particle sizes are in a range of about 35-65 nm in diameter.

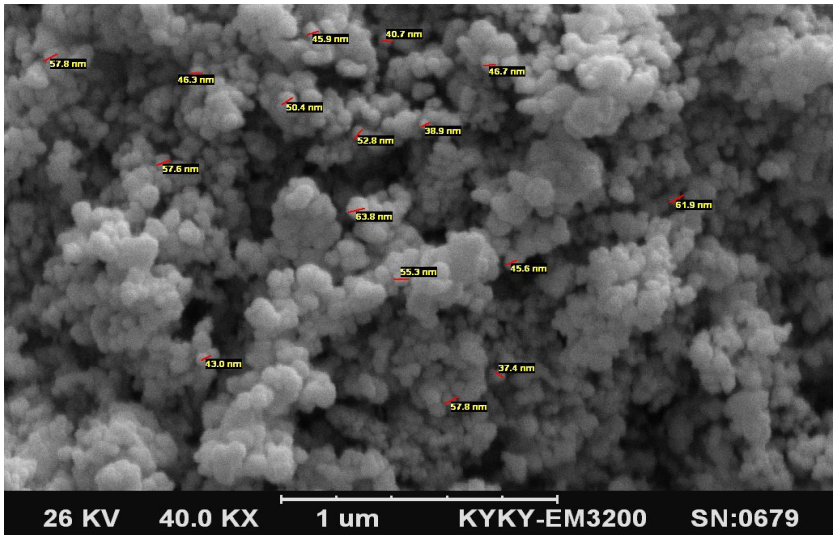
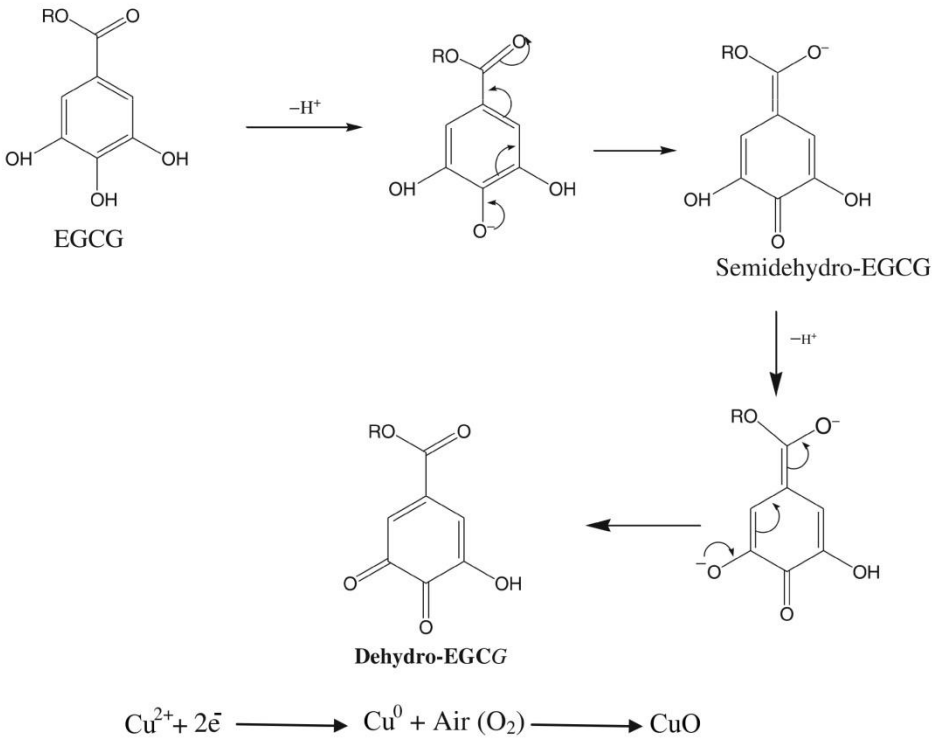


Figure 3. SEM image of CuO nanoparticles.

The role of black tea in synthesis copper oxide nanoparticles

The black tea extract was used as reducing as well as stabilizing agent for CuO nanoparticles. The possible mechanism is shown in the Scheme 1. This gives strong evidence for the involvement of polyphenols in the rapid biosynthesis and for the stability of metallic nanoparticles in the aqueous medium [22, 27]. It suggests that well dispersed copper nanoparticles may have obtained through the reduction of Cu^{+2} using tea extracts that contains epigallocatechin gallate (EGCG), which acts as both the reducing and capping agent. EGCG is a highly water-soluble compound with strong polarity. As illustrated in Scheme 1, EGCG served as a stable (electron + proton) donor during interactions. It was first converted into the radical ion ‘‘semihydro-EGCG’’ and then into dehydro-EGCG through oxidation. DehydroEGCG and EGCG together constituted the redox system which was sufficient to reduce Cu^{2+} to Cu [28]. The lone pair electrons in the polar groups of EGCG can occupy two sp orbits of the copper ion to form a complex compound. The EGCG was capped with copper ions, then synthesized Cu(0) nanoparticles through reduction of Cu^{2+} inside the nanoscopic templates. In the presence of nanoscopic templates, small copper nanoparticles were easily formed. The other explanation may be attributed to the dispersion effect of the oxidation product of EGCG

on the copper nanoparticles after the completion of the reduction reaction. EGCG was converted into dehydro-EGCG through oxidation.



Scheme 1. A proposed mechanism for the formation of CuO nanoparticles.

Conclusions

In summary, we have reported for the first time, the use of black tea powder extract for the synthesis of CuO nanoparticles using water as solvent by the green method. From XRD results, it was observed that all of the calcined CuO-NPs at different temperatures indicating the formation of single-phase CuO with a monoclinic structure. This method is interesting in applying and extending the green chemistry rules in preparation of nanoparticles. The other advantages of the method are simple synthesis, in a normal atmosphere, and low cost, giving a potential avenue for further practical scale-up of the production process and applications. The size and morphology of the samples were characterized using scanning electron microscopy (SEM).

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