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Green Synthesis of Copper Nanoparticles Using Flower Extracts: A Promising Route for Enhanced Microelectronics Packaging

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This works aims to prepare a highly dispersible, high electrical and thermally conductive, low cost copper nanoparticles, with an average particle size of 30–40 nm, by reducing an aqueous solution of copper(II) solution through bio-route using leaves of senna auriculata (Cassia Auriculata flowers). The resultant copper nanoparticles (CuNPs) possess a reduction in melting point which can be suitably used as a conductive copper nanoink material for printed circuitry boards and also as a low-cost replacement for silver and gold nanoinks in inkjet printing of conductive patterns. The green-synthesized CuNPs are characterized using FT-IR, UV-Visible, and photoluminescence studies and scanning electron microscopic (SEM) and X-ray diffraction studies. All the obtained results confirmed the presence of copper nanoparticles in the sample. The prepared CuNPs is expected to provide promising advances as nanopastes for sustainable fabrication of copper electrodes and die attachment materials for the production of next-generation power semiconductors.

Keywords: Senna auriculata; CuNPs; SEM; TEM; nanoinks.

1. Introduction

Nanoparticle production has received a lot of attention in recent years due to its enormous potential for replacing pricey nanosilver inks used in conductive printing.[1] The intrinsic tendency of copper nanoparticles to oxidize under ambient settings is a key challenge when using them. Electronic packaging of vehicle electronics by high melting metallic components plays a critical role in automobile design. Nano Copper-based materials are beneficial for automobile electronics packaging.[2,3] They serve as the foundation for power module connectors, die attach joints, electrical contacts, and substrate attach material. However, they are detrimental to the environment and do not meet with hazardous substance restrictions. Sintered Copper has been discovered to be a superior option. It has a high melting point and excellent electrical and thermal conductivity. The organic coating will evaporate during sintering, resulting in the creation of strong Cu joints or packing.[4] After sintering, the high melting temperature of the bulk Cu (960°C) can be seen in these joints. It has been found that as the sintering temperature rises above 200°C, the joint strength increases.

In this study, we propose a method to make Cu nanopastes that can endure the ambient operating conditions of car electronics while sintering and producing strong joints. Copper dietary supplements with a high rate of absorption, EMI shielding with high-strength metal, alloys, Cu nanoparticle-based conductive inks and pastes can be utilized to replace pricey noble metals in printed electronics, displays, and transmissive conductive thin film applications.

In this work, an ecologically friendly technique introduces a new way of thinking in chemistry with the goal of eliminating hazardous waste, reducing energy usage, and using environmentally friendly solvents.[5] The advantage of greener synthesis of nanoparticles over chemical route is that the nanoparticles produced have a more diversified nature, higher stability, and appropriate size and they are synthesized using a one-step procedure.[6] To avoid the production of unwanted or harmful by-products through the build-up of reliable, sustainable, eco-friendly synthesis procedures.[7]

2. Materials and Methods

All the chemicals were purchased from Merck Ltd (almost 99.99% purity) and utilized without additional purification for the synthesis of copper nanoparticles. The process involved dissolving polyvinylpyrrolidone K30 (0.02 M) in 100 mL deionized water, which was mixed with the aqueous extract of senna auriculata flowers. Ascorbic acid (0.02 M) was added as an antioxidant of colloidal copper, followed by the gradual addition of copper (II) sulfate pentahydrate solution (0.01 M) under continuous stirring. Adjusting the pH to 10 was achieved by adding ammonia solution (25%). The change in color from white to reddish brown indicates the initiation of the reaction, which was allowed to proceed for 60 min under rapid stirring in ambient conditions. The melting temperature of the green synthesized CuNPs was observed around 650°C.

3. FT-IR Spectral Analysis

Fourier transform Infrared Spectroscopy (FTIR, Model 8400S, Shimadzu, Japan) was used to perform the FT-IR study for the synthesized CuNPs using potassium bromide (KBr) pellet method within a predetermined spectrum range of 4000–400 cm^{-1}.[8] Figure 1 shows the FTIR spectra of the CuNPs. The stretching modes of O–H in CuNPs and water were visible in the peaks at the wave number range of 3740 cm^{-1}. Additionally, C–H stretching vibrations are considered to be the cause of the peak at the 2883 cm^{-1}.[9] The >C=O stretching, –C=C– stretching, –OH stretching, and C–O stretching vibrations, respectively, were also shown by the peaks at 1643.24 cm^{-1}, 1547.77 cm^{-1}, 1291.25 cm^{-1}, and 1073.31 cm^{-1} indicated that the

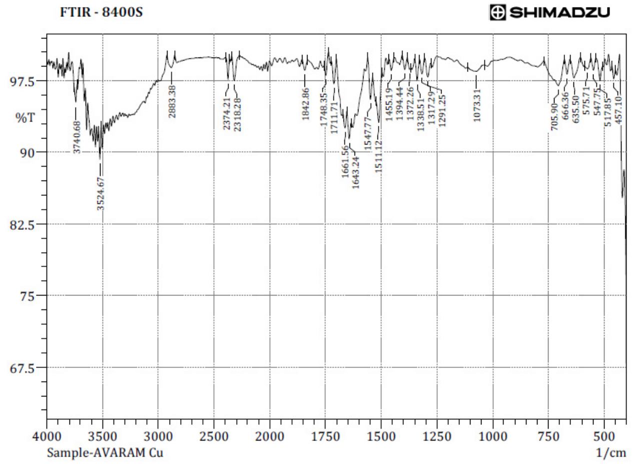


Fig. 1. FT-IR spectrum of the CuNPs (in liquid form) synthesized using Sena auriculata leaves extract.

extract contained anthraquinone moiety. The peak at 2883.38 cm^{-1} indicated that the extract contained phenolic and flavonoid acids. The presence of flavonoids and phenolic functional groups in the extract may be related to the reduction of metal ions and the creation of the corresponding nanoparticles.[10] On the surface of the nanoparticles, flavonoids and phenolic functional groups may be adsorbed. This is most likely accomplished by interacting through π-electrons in the absence of other powerful ligating agents.[11]

4. UV-Vis Spectral Analysis

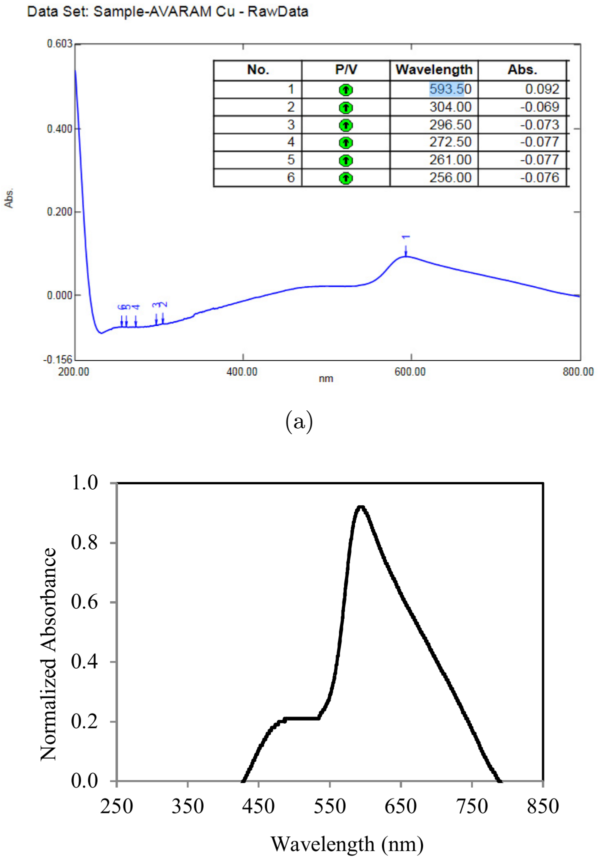
Applying an UV-VIS spectrophotometer with a wavelength range of 200–800 nm, the absorbance spectra of the CuNPs generated using the Cassia Auriculata, *Cinnamomum verum, Catharanthus roseus*, and *Ocimum tenuiflorum* extracts were separately examined and given in Table 1.[12]

The extract's UV spectrum revealed absorbent bonds relating to the rings of the benzoyl and cinnamoyl systems, respectively, at 244 nm and 377.5 nm. These connections show the existence of polyphenolics via relating to the π–π transitions.[13] Similar to this, Cu nanoparticles' claimed absorption bands have been reported in the literature to be between 550 nm and 650 nm.[14] After reduction, the colloidal suspension showed one surface plasmon resonance (SPR) at a wavelength of 593.5 nm, confirming that copper nanoparticles had formed as shown in Fig. 2.

The SPR band represents a collective oscillation of free electrons at the surface of copper nanoparticles upon excitation by incident light.[8,15] This resonance induces a prominent absorption peak at 593 nm and results in light scattering at a specific wavelength of 613 nm, both of which are intricately linked to the nanoparticles' size. In the case of copper nanoparticles, SPR predominantly occurs within the visible to near-infrared range of the electromagnetic spectrum.

Table 1. UV–visible and photoluminescence data of the green-synthesized CuNPs.

Biosynthesized copper nanoparticles		
Extract used	UV data (nm)	PL (nm)
Cinnamomum verum	464, 366, 347	737
Ocimum tenuiflorum	No intense peak	737
Catharanthus roseus	354, 342, 279	712
Cassia auriculata	593	613
PVP	213.5, 371	394
$CuSO_4 \cdot 5H_2O$ (Bulk)		818



No.	P/V	Wavelength	Abs.
1	↑	593.50	0.092
2	↑	304.00	-0.069
3	↑	296.50	-0.073
4	↑	272.50	-0.077
5	↑	261.00	-0.077
6	↑	256.00	-0.076

(a)

(b)

Fig. 2. (a) UV-Visible spectrum of the CuNPs synthesized with absorption around 593.5 nm. (b). Surface plasmon absorption bands for the synthesized CuNPs.

5. Photoluminescence Analysis

From the PL spectra, it is observed that, smaller size of the nanoparticles will lead to blue shift at 613 nm (lower wavelength), when compared to longer wavelength for the larger size nanoparticles. Hence, it is concluded that, a blue shift was observed for the CuNPs synthesized using Cassia Auriculata extract as shown in Fig. 3.

A variety of herbal species including Cassia Auriculata, *Cinnamomum verum*, *Syzygium aromaticum*, *Ocimum tenuiflorum*, and Nithyakalyani flowers were used to stabilize the copper nanoparticles (CuNPs) photoluminescence spectra. Out of all the above-mentioned species, we are able

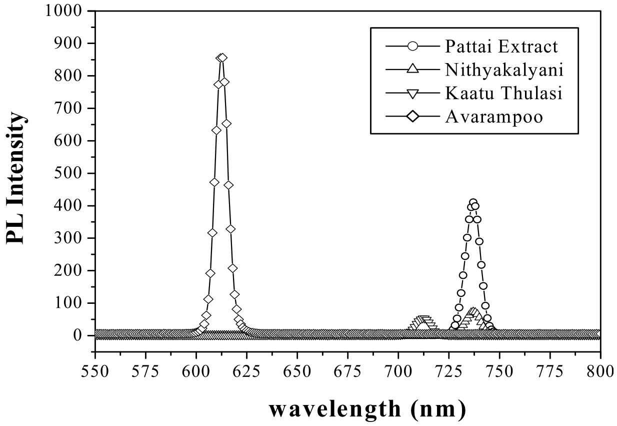


Fig. 3. Photoluminescence spectrum of the green-synthesized CuNPs using various flower extracts.

to produce a spectrum with an emission peak at approximately 613 nm (a close agreement with the literature report). The first electronic relaxation that follows the radiative recombination of an electron–hole pair between the d-band and the SP-conduction band is what causes the photoluminescence phenomenon. The photoluminescence behavior of copper, where 3d valence and 4s 4p conduction electrons play a key role, is explained by the electrical structure of copper. This photoluminescence activity results from the recombination of the electron–hole pair between the d-band and sp-conduction band followed by initial electronic relaxation. CuNPs as-prepared show an interesting peak in the photoluminescence spectra at 613 nm. The reaction medium's maximum was found to correspond to the excitation spectrum (SPR at 613 nm). X-ray diffraction has been used to confirm the structure identification because it is possible that the reduction of the Cu^{2+} may result in the preferential production of CuNPs over CuO. The chemical composition of the biosynthesized CuNPs has been verified using X-ray diffraction studies (Fig. 4).

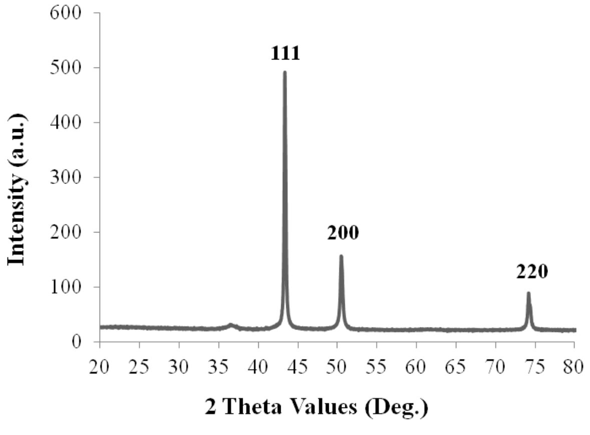


Fig. 4. XRD spectrum of the biosynthesized CuNPs (matching with the literature JCPDS 04-0836).

6. SEM Analysis

The SEM image displays the size of the CuNPs with almost spherical forms and sizes typically less than 50 nm and are visible in the SEM image[16,17] as shown in Fig. 5.

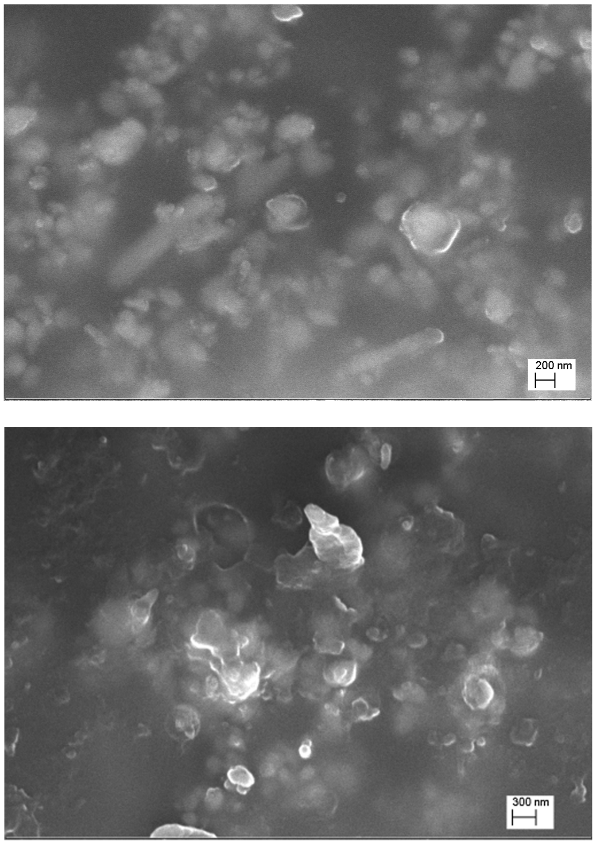


Fig. 5. SEM image of the synthesized CuNPs (before (top) and after sintering (bottom)).

7. XRD Analysis

The size of the generated nanoparticles is influenced by variations in plant species, reducing agents found in extracts, and process parameters. The copper peaks in the copper nanoparticles were detected by EDX analysis as given in Fig. 6. Due to the glass components used in the coating process, peaks for Si, Ca, Mg, Al, and C were also obtained in the result.

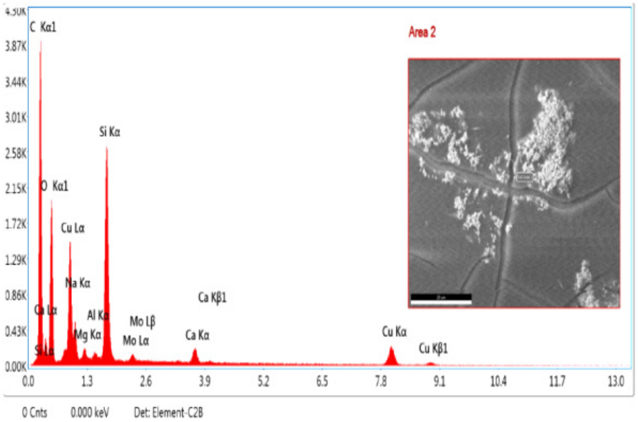


Fig. 6. EDX spectrum of the synthesized CuNPs.

This study investigated the use of natural extracts from five different plant species: Cassia auriculata, *Cinnamomum verum* (Cinnamon), *Catharanthus roseus* (Madagascar Periwinkle), and *Ocimum tenuiflorum* (Holy Basil) for synthesizing copper nanoparticles. Among these extracts, Cassia auriculata was identified as particularly effective in producing copper nanoparticles with smaller size of 30–40 nm.

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