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Ultrasonic Assisted Facile Synthesis of CuO Nanoparticles and Used as Insecticide for Mosquito Control

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The present study deals with the fabrication of copper oxide nanoparticles with high purity *via* ultrasonic assisted chemical precipitation method. Synthesized CuO nano-mosquitocides rely on the polyvinyl pyrrolidine (PVP) as stabilizing agent. Synthesized CuO nanoparticles were confirmed *via* UV-vis spectroscopy, scanning electron microscope, X-ray diffraction, EDX, Fourier-transform infrared and SEM mapping studies. The crystallite size from XRD studies revealed around 13.44 nm. The synthesized CuO nanoparticle was further assessed for mosquito larvicidal activity against south-urban mosquito larvae *Aedes aegypti*. The synthesized CuO nanoparticle displayed significant activity against *Aedes aegypti* with the LD_{50} value of 43.95 µg/mL than precursor copper chloride dihydrate and control permethrin with the LD_{50} value of 94.31 and 72.44 µg/mL.

Keywords: *Aedes aegypti*, CuO nanoparticles, Larvicidal activity.

INTRODUCTION

For mosquito control, chemical insecticides are utilized, however they are toxic to non-target species and causing humanoid health issues [1]. Efficient and environmentally sustainable management mechanisms must therefore be targeted in order to efficiently manage this issue. Biopesticides may be developed in order to successfully track mosquitoes *via* several mechanisms [2]. Mosquitos spread awful illnesses and pathogens globally, like malaria, dengue, filariasis, hemorrhagic fever, *etc*. Mosquitoes are widespread and trigger almost two million lives annually [3]. Most of the mosquito diseases, including disruption to socio-economic and manual work in countries with subtropical and tropical areas, absorb financial power, but no earth's ecosystems environment is safe of vector-borne diseases [4]. *Anopheles stephensi* is India's main malaria vector. Malaria has become one of the largest significant infectious illnesses with an occurrence measured at 300-500 million under health manifestations though with a past squeak of approximately 1.1 and 2.7 million. Still, almost 40% of people residing in the biosphere live in tropical malaria places [5]. The lymphatic filariasis vector of *Culex quinquefasciatus*, which is commonly distributed by rainfall, is a recurrent phenomenon in the world for between 120 million and 44 million people [6].

Metal oxide nanocrystals are of particular interest due to their unique characteristics that set them apart from bulk materials, including a greater surface area to volume ratio, enhanced chemical reactivity, specialized electronic properties, and remarkable optical properties [7-9]. The synthesis of copper monoxide at the nanoscale earned surprise little coverage relative to other transition metal oxides. CuO is, however, a p-type semi-conductive with a tight bandwidth, the scale of the bandwidth depends significantly on the material's morphology and particle size [10]. For superconductors and antiferromagnetic semiconducteurs, CuO has become important [11]. Other uses include solar cells [12], gas sensors [13] and magnetic storage media [14-16] and as a heterogeneous catalyst [17]. Different synthetic routes have been used to manufacture CuO nanoparticles, including sol-gel processing [18], solid-state synthesis at low temperature [19,20], co-implantation tech-

niques [21], electrochemical lines [22], microwave irradiation [23,24], hydrothermal [25] and thermal degradation [26,27]. In the meantime, the formation mechanism *via* $Cu(OH)_2$ was already identified very well [28-32]. When the reagents were heated in an autoclave at 140 ºC for 20 h [33], copper oxide nanoplatelets were collected from a combination of ionic liquid ([C4mim]Cl) and water.

Sonochemistry has been a strong tool for the synthesis of nanoparticles in recent years [34-37] and used in the fabrication of CuO nanoparticles [38]. There has been detailed analysis into the sonochemical synthesis of nanocrystalline CuO in poly(vinyl alcohol) (PVA) and the impact of PVA on CuO development [39]. While a substance is exposed to ultrasound bubbles, they implode and grow. This results in extraordinarily high temperatures, stresses and cooling speeds locally [40]. Recently, ZnO nanorods were also synthesized with simple way to access by incorporating the benefits of both room-temperature ionic fluids (RTILs) and ultrasound synthesis [41]. A highly selective, simple route is described here for the development of CuO nanoparticles from copper(II) chloride dihydrate in ethanol by ultrasound-assisted synthesis.

EXPERIMENTAL

All materials were purchased from Nice and Loba chemicals. Solvents used during the reactions were of high purity and utilized without further purification.

Synthesis of copper oxide nanoparticles: Copper(II) chloride dihydrate (0.05 g) was dissolved in 30 mL of ethanol and stirred using a magnetic stirrer. After 10 min of stirring, 0.05 g of polyvinyl pyrrolidine (PVP) was added to the reaction mixture and stirred continuously. After 20 min stirring, 0.5 M NaOH solution was added dropwise. Then, the reaction mixture was subjected to sonication (32 kHz@100 W) for 2 h. Finally, the obtained precipitate was centrifuged at 6000 rpm with repeated washing of water and ethanol to eliminate NaCl from the final product. The powder obtained was crushed using pestle mortar into fine powder. The synthesis sequence is illustrated in **Scheme-I**.

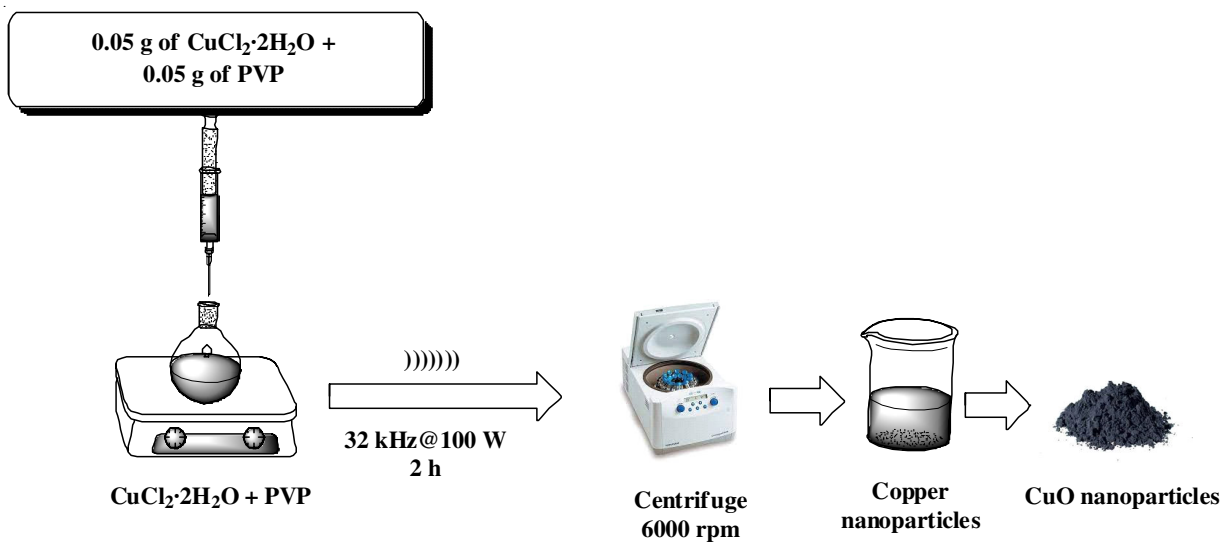
Characterization: Copper oxide nanoparticles synthesized by using the ultrasonic assisted chemical precipitation technique. UV-Visible spectra was recorded with V-730 UV-visible spectrophotometer at a wavelength ranges between 200-800 nm. FT-IR spectrum was recorded with Fourier transform infrared spectrometer (FT/IR-6600) (CHI 1000C) in the range 4000-400 cm^{-1}, Powder XRD was assessed with X'Pert Pro by PANalytical, FE-SEM with EDX and Mapping were done with FESEM sigma essential by Zeiss microscopy.

Larvicidal activity: The synthesized CuO nanoparticle was further assessed for larvicidal activity against south urban mosquito larvae *Aedes aegypti*. Appraisals were made on a dead/alive premise. Assessments depend on a rate size of 0-100, which 0 equivalents no action and 100 equivalents complete murder. The bioassay was rehashed multiple times and the consequence of bioactivity was the normal of these reproduces. The qualities are contrasted and the positive control permethrin. The LD_{50} values of some dynamic title mixtures were assessed utilizing probit investigation and the outcomes were dissected utilizing the SPSS v16 programming.

Larvicidal activity against mosquito (*Aedes aegypti*): The precursor copper chloride dihydrate and combined CuO nanoparticle were assessed for larvicidal activity against south urban mosquito larvae *Aedes aegypti*. The assessment of larvicidal activity at the starter test convergence of 100 µg/mL in contrast to the 4th instar south-urban mosquito larvae *Aedes aegypti* through water immersion strategy beneath relative stickiness 50-70%, photoperiod of 10:14 (light:dark) and temperature of 27 ± 2 ºC. The tests were set up at the convergences of 100, 75, 50, 25 µg/mL by utilizing DMSO. All the test measuring glasses comprising 20 *Aedes aegypti* were assessed for 24 h later handling. The outcomes were documented by average percent mortality.

RESULTS AND DISCUSSION

Optical studies: The reduction of Cu^{2+} ions to Cu^0 nanoparticles was visually observed by colour variation in the reaction mixture. The gradual colour change in solution from light green



Scheme-I: Ultrasonic assisted synthesis of CuO nanoparticle

to sky blue. This indicates that the metal chlorides were reduces to form its respective nanoparticles.

UV-visible studies: The UV-visible absorption peak arises from 200-400 nm denote the development of CuO nanoparticles. In present study, the extreme absorption peak seemed at 390 nm directs the individual SPR peak for CuO NPs with lesser particle size. Fig. 1 displays the UV-vis spectra of CuO nanoparticles synthesized by sonication protocol.

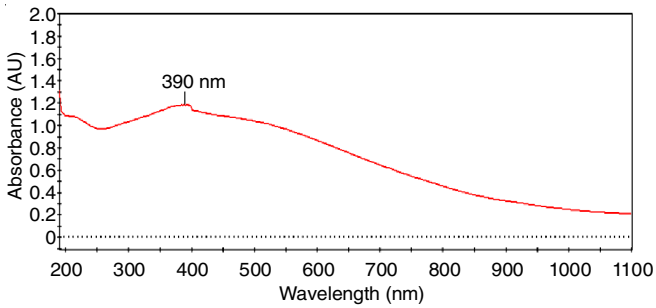


Fig. 1. UV-visible spectra of CuO nanoparticle

FTIR studies: FT-IR spectrum of the synthesized CuO nanoparticles is shown in Fig. 2. The O-H group has a broad rise at 3239.95 cm^{-1}, which may have been caused by the appearance of the hydroxyl moiety [42]. The bands at 3000-2800 cm^{-1} signify the existence of C-H functional group of alkanes [43]. The peak at 1626.66 cm^{-1} showed the incidence of carbonyl moiety (C=O) due to atmospheric CO_2 [44], while the band at 567.00 cm^{-1} approves the existence of Cu-O vibrations [42]. FT-IR analysis confirmed the existence of functional groups in the capping agent and also the formation of CuO NPs.

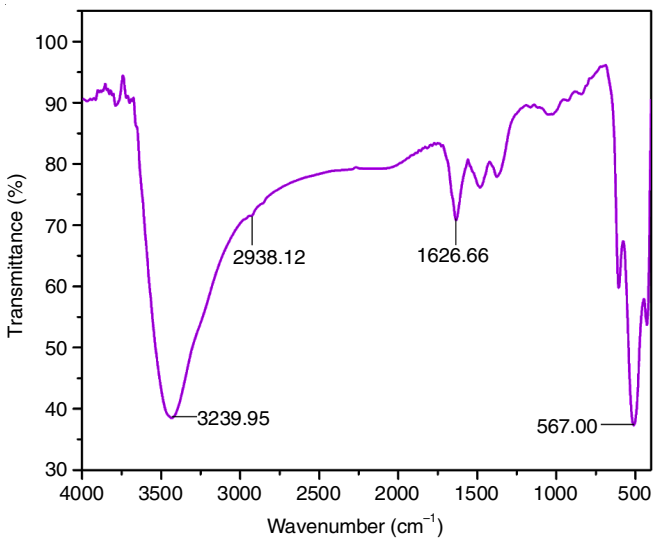


Fig. 2. FT-IR spectra of CuO nanoparticle

SEM and mapping studies: SEM image shown in Fig. 3 confirmed that the obtained CuO nanoparticles were sponge like morphology. The CuO nanoparticles were dispersed as distinct particles and monodispersivity in nature. The SEM mapping (Fig. 4) studies also conforms the synthesized nanoparticle was CuO. The blue dots corresponds to copper atom and rose dots represents oxygen atom.

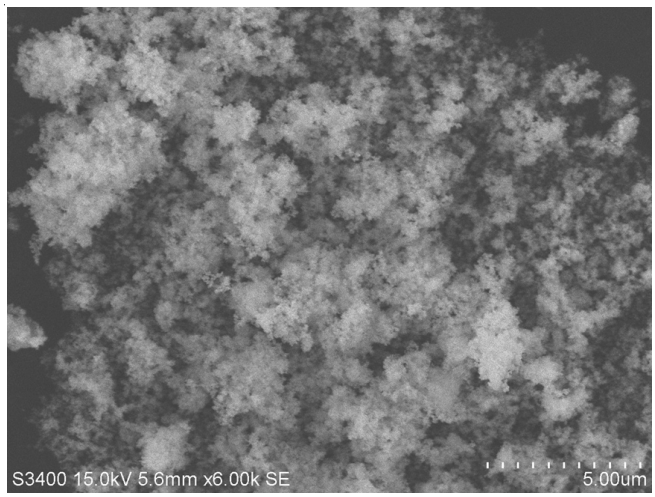


Fig. 3. SEM image of CuO nanoparticle

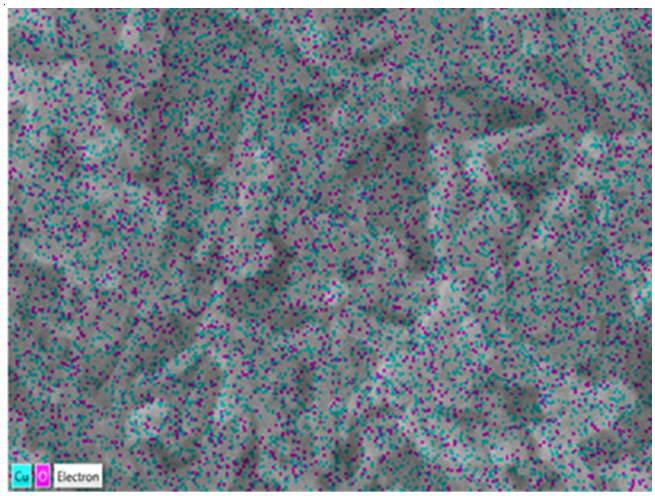


Fig. 4. SEM image mapping of CuO nanopaticle

EDX studies: The EDX spectra showed that the synthesized material was indeed CuO nanoparticles, as expected from the presence of copper and oxygen peaks (Fig. 5). The weight percentage of copper and oxygen atoms were 65.87 and 34.13, respectively. The further peaks extant in the spectra may be as a result of the existence of bioorganics or impurities in the solution. The elemental composition of CuO nanoparticle is shown in Table-1.

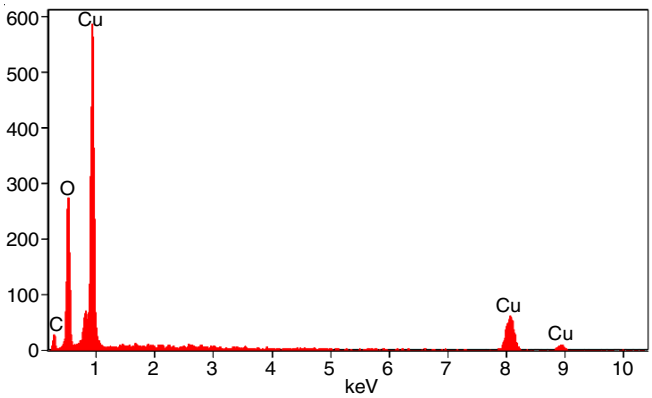


Fig. 5. EDX spectra of CuO nanoparticle

TABLE-1
ELEMENTAL COMPOSITION OF CuO NANOPARTICLE

Element	Atomic number	Weight (%)	Atom (%)	Weight (%) error
O	8	34.13	67.94	7.4
Cu	29	65.87	32.06	5.2
Total	–	100.00	100.00	–

XRD studies: The XRD pattern of the sonicated derived CuO nanoparticles is shown in Fig. 6. The diffraction peaks at 2θ = 32.5º, 35.5º, 38.7º, 44.2º, 48.8º, 53.5º, 58.3º, 61.6º, 66.2º, 68.0º, 72.4º and 75.1º are respectively indexed to (110), (111), (111), (112), (202), (020), (202), (113), (310), (220), (311) and (310) planes of monoclinic structure of CuO nanoparticle. The obtained diffraction peaks were matched with of standard CuO NPs. All the diffraction peaks were in good agreement with the standard pattern for pure monoclinic phase of copper oxide nanoparticles (JCPDS No. 80-0076) and no contaminant peaks were found. The strong peaks imply that the produced nanoparticles are very crystalline. The Debye-Scherrer equation (eqn. 1) may be used to compute the average crystallographic size from the recorded primary diffracted peak.

$$D_{(hkl)} = \frac{k\lambda}{\beta\cos\theta}$$

where $D_{(hkl)}$ is the average crystalline size, β is the full width half maximum (FWHM), k is the shape constant (0.89), θ is the X-ray incidence angle and λ is the incident X-ray wavelength (λ = 0.15405 nm). The synthesized CuO nanoparticles had an average crystallite size of 13.44 nm.

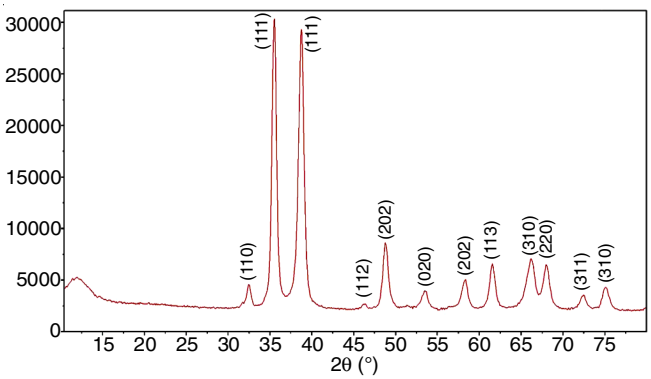


Fig. 6. XRD spectra of CuO nanoparticle

Larvicidal activity: The synthesized CuO nanoparticle was extremely active in contradiction of *Aedes aegypti* with the LD_{50} value of 43.95 µg/mL than precursor copper chloride dihydrate and control permethrin with the LD_{50} value of 94.31 and 72.44 µg/mL. Among the test samples, precursor copper chloride dihydrate displayed less action towards *Aedes aegypti* with the LD_{50} values of 94.31 µg/mL. The synthesized CuO nanoparticle was highly active and precursor copper chloride dihydrate was moderately active compared to the positive control permethrin with the LD_{50} value of 72.44 µg/mL. The results are shown in Table-2.

Conclusion

The current study highlights the ultrasonic assisted chemical precipitation approach for the synthesis of CuO nanoparticles is reported. Synthesized CuO nanoparticles were confirmed *via* UV-vis spectroscopy, Fourier-transform infrared spectroscopy, X-ray diffraction, scanning electron microscope, SEM mapping and EDX studies. In addition, CuO nanoparticle was further evaluated for the larvicidal activities. The synthesized CuO particle displayed significant activity against *Aedes aegypti* with the LD_{50} value of 43.95 µg/mL than precursor copper chloride dihydrate and control permethrin with the LD_{50} value of 94.31 and 72.44 µg/mL. Consequently, CuO nanoparticles might be a probable basis for emerging environmentally friendly bioactive compound, as well as ecological biopharmaceuticals and insecticides.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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TABLE-2
LARVICIDAL ACTIVITY OF PRECURSOR COPPER CHLORIDE DIHYDRATE AND SYNTHESIZED CuO NANOPARTICLE

Compd. No.	Mortality (%)/Concentration (µg/mL)[a]				LD_{50} (µg/mL)
	100	75	50	25	
Copper chloride dihydrate	55.27 ± 0.07	38.03 ± 0.10	29.10 ± 0.13	13.16 ± 0.11	94.31
CuO nanoparticles	84.71 ± 0.13	70.01 ± 0.19	52.62 ± 0.21	28.60 ± 0.22	43.95
Permethrin	70 ± 0.67	46 ± 1.29	30 ± 1.78	16 ± 0.98	72.44
DMSO	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0	0.0 ± 0.0

[a]Value were the means of three replicates ± SD.

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