LEAVES AND FRUITS EXTRACTS OF *TAMARIND INDICA* L (MA-GYI) MEDIATED SYNTHESIS OF COPPER(II)OXIDE NANOPARTICLES AND THEIR CHARACTERIZATIONS

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Abstract

Leaves and fruits extracts of *Tamarindus indica* L. (Ma-Gyi) mediated synthesis of copper(II) oxide nanoparticles (CuO NPs) were conducted in this research. Formation of CuO nanoparticles was studied at four different temperatures *viz*., 200 ºC, 300 ºC, 400 ºC and 500 ºC and CuO particles formed were characterized by X-ray diffraction analysis. At the temperature of 200 ºC, formation of Cu_2O was observed. As the temperature was increased to 300 ºC most of Cu_2O particles converted to CuO and at 400 ºC Cu_2O impurities peaks were still observed. At 500 ºC, all of the Cu_2O peaks disappeared and only single phase of CuO nanoparticles was observed. Well- dissolved characteristic peaks such as (110), ($\bar{1}$11), (111), ($\bar{2}$02), (020), (202) and ($\bar{1}$13) of CuO nanoparticles were found in XRD pattern. CuO nanoparticles were indexed as monoclinic with crystallite sizes of 19.9 nm and 20.9 nm calculated by Scherrer equation. The crystallite sizes of CuO NPs obtained by using leaves and fruits extracts of *T. indica* L. were found to be 21.2 nm and 21.7 nm, respectively by TEM analysis. SEM analysis showed a large number of spherical nanoparticles with dense agglomerates. Thermal analysis of CuO nanoparticles showed that CuO was almost thermally stable beyond 400 ºC. The presence of characteristic vibration of Cu-O in the range of 430-606 cm^{-1} was confirmed by FT IR analysis.

Keywords: *Tamarindus indica* L., copper(II) oxide nanoparticles, monoclinic, Scherrer equation

Introduction

Metal oxides are the most diverse group in chemistry as their special properties covered nearly all aspects in both science and technology. Among various metal oxides, transition metal oxides are the most technologically advanced and economically attractive. Copper(II) oxides nanoparticles (CuO NPs) are of interest because it issimple, highly stable, relatively more cost effective than other metals like gold and silver, stable over a wide range of pH and high temperature resistance. CuO NPs were found to be extremely useful in wide variety of applications such as antimicrobial agent (Ren *et al*., 2009), photocatalyst (Katwal *et al*., 2015), solar cells (Kitowaki *et al.,* 2012), lithium ion battery (Thi *et al.,* 2014) and gas sensor (Zhang *et al*., 2011). Nowadays, CuO nanoparticles are utilized as heterogeneous catalysts, antioxidants, drug delivery agents, and imaging in field of biomedicine (Faheem *et al.,* 2017).

Copper(II) oxide nanoparticles can be synthesized by various chemical methods such as sol-gel method (Etefagh *et al*., 2013), precipitation (Phiwdang *et al*., 2013), hydrothermsynthesis (Outokesh *et al.*,2011), chemical reduction, thermal decomposition, electrochemical method (Ghorbani, 2014) and wet chemical method (Joshua *et al.,* 2014). However, these chemical methods have disadvantages e.g., the release of hazardous chemicals and absorption of some toxic chemicals on surface of nanoparticles. So a convenient, rapid, mild , non-toxic and natural product to produce copper oxide in aqueous environment is required. Green synthesis of metal oxide nanopatilcles involves using bacteria, fungi, algae and plants. Among them nanoparticles synthesized from plants are more stable, inexpensive, faster than in the case of microorganisms. So, this study is aimed to synthesize CuO NPs from $Cu(NO_3)_2$ by using leaves and fruits extracts of *Tamarindus indica* L. (Ma-Gyi) which is readily available in Myanmar.

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Materials and Methods

Samples Collection

The *Tamarindus indica* L. (Ma-gyi) leaves and fruits were collected from Leindaw village, Meiktila Township, Mandalay Region.

Preparation of Copper(II) Oxide Nanoparticles

Copper(II) oxide nanoparticles were prepared by dropwise addition of 50 mL 0.5 M copper(II) nitrate solution into 25 mL of extracts sample solution in a 250 mL beaker and then mixed thoroughly by a magnetic stirrer at 60 ºC. The deep blue colour of solution changed to dark green and it was heated at 80 ºC. The dried sample was then collected and calcined in a muffle furnace at 200, 300, 400 and 500 ºC for 1 h. A black coloured powder was obtained and it was carefully collected and packed for characterization purposes.

Characterization Techniques

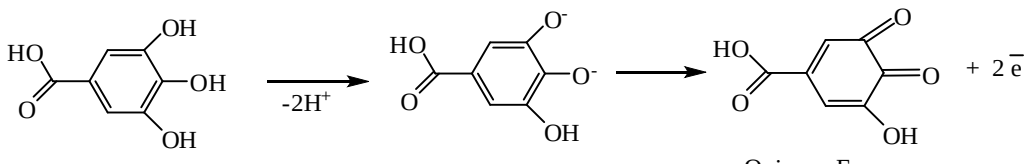
The crystalline structure and phase purity of the synthesized CuO NPs were examined by using X-ray diffractometer (Rigaku Co., Tokyo, Japan) using Cu Kα (λ=1.54056 Å) radiation in a scattering range (2θ) of 10° to 70° at an accelerating voltage of 40 kV. The morphologies of CuO NPs were characterized by scanning electron microscopy (SEM, JEOL-JSM-5610 LV, Japan) at Universities' Research Center, Yangon and transmission electron microscopy (TEM, JEOL TEM-3010) with an accelerating voltage of 100 kV at State Key Laboratory, College of Science , Beijing University of Chemical Technology, China. The crystallite sizes of CuO NPs were calculated by using Image J software programme. TG-DTA (DTG-60H) Thermal Analyzer, SHIMADZU, Japan was employed for investigation of the thermal property of the synthesized samples. Fourier Transform (FT IR) spectra of copper(II) oxide samples were recorded on a FT IR spectrometer (FT IR-8400 SHIMADZU, Japan).

Results and Discussion

Mechanism for the Bioreduction of Cu^{2+} to CuO Nanoparticles

T. indica leaves and fruits contain polyphenolic compounds, for example gallic acid. These phenolic compounds have high reducing ability and they involve in bioreduction of Cu^{2+} to Cu_2O. Then Cu_2O was oxidized in air to produce CuO NPs. These phenolic compounds act as reducing as well as capping agents (Sharma *et al*., 2015). The proposed mechanism for the bioreduction of CuO is shown as follows:

$$Cu(NO_3)_2 \longrightarrow Cu^{2+} + 2NO_3^-$$



Gallic Acid (Phenolic Form) — Quinone Form

$$2\,Cu^{2+} + 4\bar{e} + \frac{1}{2}O_2 \longrightarrow Cu_2O \text{ (reduction)}$$

$$Cu_2O + \frac{1}{2}O_2 \text{ (air)} \longrightarrow 2CuO \text{ (oxidation)}$$

Characterization of the Prepared CuO NPs by XRD Analysis

Copper(II) oxide nanoparticles obtained by using leaves and fruits extracts of *T. indica* were characterized by X-ray diffraction analysis. X-ray diffraction patterns of the prepared copper(II) oxide nanoparticles at 200 ^{o}C are shown in Figure 1. Formation of Cu_2O instead of CuO was observed in the XRD pattern of copper oxide obtained by using leaves extract of *T.indica.* Phase identification of X-ray analysis shows a single phase of Cu_2O (Table 1). Furthermore, well-defined peaks were not observed in the XRD pattern of copper oxide obtained by using fruits extract of *T. indica*. Table 2 shows both CuO phase and Cu_2O phase in copper oxide obtained by using fruits extract . Increase the temperature to 300 ^{o}C and 400 ^{o}C, the diffraction peaks of CuO NPs obtained by using leaves and fruits extracts of *T. indica* were found to be well- resolved and most of Cu_2O particles were converted to CuO. However, Cu_2O peaks were still observed at these temperatures (Figures 2 and 3). At 500 ^{o}C, Cu_2O peaks disappeared in both samples obtained by using leaves and fruits extracts of *T. indica* and only single phase of CuO was observed (Figure 4). The XRD patterns show no impurity peaks. Prominent diffraction peaks of CuO were observed at 2θ values of 35.308^{o} and 38.518^{o} using leaves extract and 35.287 ^{o} and 38.473 ^{o} using fruits extract corresponding to the Miller indices of $(\bar{1}11)$ and (111) respectively. Comparison of X-ray diffractograms of copper(II) oxide nanoparticles by using leaves and fruits extracts at different temperatures are shown in the overlay of x-ray diffractograms (Figures 5 and 6). It was observed that as the temperature increased the diffraction peaks became well defined and the peaks corresponding to Cu_2O peak at 2θ of 29.444 ^{o} , 36.303 ^{o} , 42.069 ^{o} and 52.396 ^{o} disappeared.

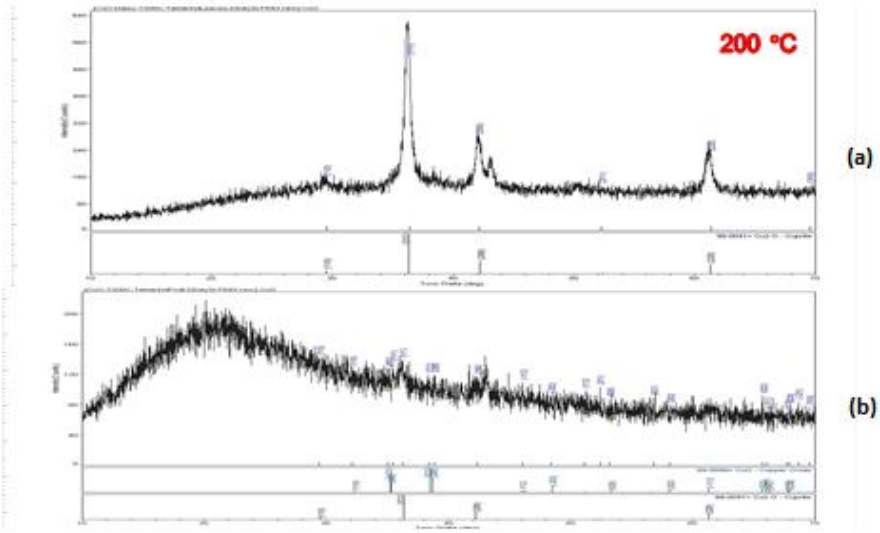


Figure 1 X ray diffractogram of the prepared CuO NPs by using (a) leaves extract and (b)fruits extract of *T. indica* at 200 °C

Table 1 Diffraction Angle, Interplanar Spacing and Miller Indices of the Prepared CuO NPs by Using Leaves Extract of *T. indica* at 200 °C

No.	Diffraction angle (2θ) (degree)	Interplanar spacing (Å)	Miller indices			Remark
			h	k	l	
1	29.119	3.0641	1	1	0	Cu_2O
2	36.243	2.4765	1	1	1	Cu_2O
3	42.121	2.1435	2	0	0	Cu_2O
4	52.050	1.7556	2	1	1	Cu_2O
5	61.258	1.5119	2	2	0	Cu_2O
6	69.546	1.3506	3	1	0	Cu_2O

Table 2 Diffraction Angle, Interplanar Spacing and Miller Indices of the Prepared CuO NPs by Using Fruits Extract of *T. indica* at 200 °C

No.	Diffraction angle 2θ (degree)	Interplanar spacing Å	Miller indices			Remark
			h	k	l	
1	29.437	3.0318	1	1	0	Cu_2O
2	32.176	2.7797	1	1	0	CuO
3	35.101	2.5544	0	0	2	CuO
4	35.400	2.5335	$\bar{1}$	1	1	CuO
5	36.211	2.4787	1	1	1	Cu_2O
6	38.453	2.3391	1	1	1	CuO
7	42.346	2.1327	2	0	0	Cu_2O
8	45.956	1.9732	$\bar{1}$	1	2	CuO
9	48.555	1.8735	$\bar{2}$	0	2	CuO
10	51.325	1.7787	1	1	2	CuO
11	52.397	1.7448	2	1	1	Cu_2O
12	53.157	1.7216	0	2	0	CuO
13	58.064	1.5872	2	0	2	CuO
14	61.149	1.5143	2	2	0	Cu_2O
15	61.262	1.5118	$\bar{1}$	1	3	CuO
16	65.713	1.4198	0	2	2	CuO
17	65.948	1.4153	$\bar{3}$	1	1	CuO
18	67.687	1.3831	1	1	3	CuO
19	67.915	1.3790	2	2	0	CuO
20	68.641	1.3662	$\bar{2}$	2	1	CuO

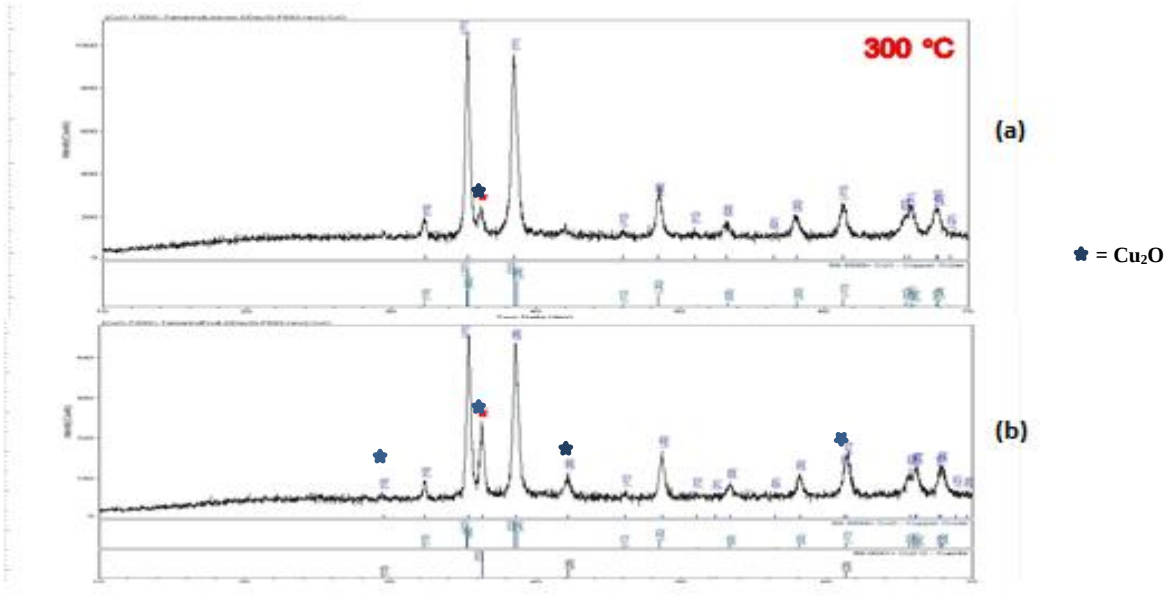


Figure 2 X ray diffractogram of the prepared CuO NPs by using (a) leaves extract and(b) fruits extract of *T. indica* at 300 °C

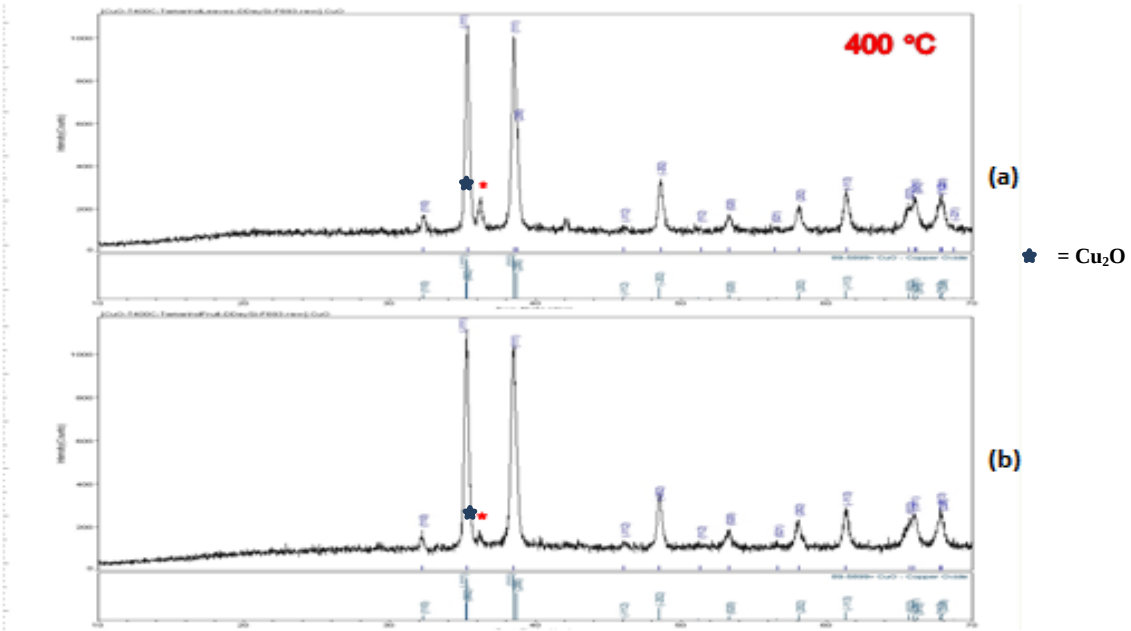


Figure 3 X ray diffractogram of the prepared CuO NPs by using (a) leaves extract and (b) fruits extract of *T. indica* at 400 °C

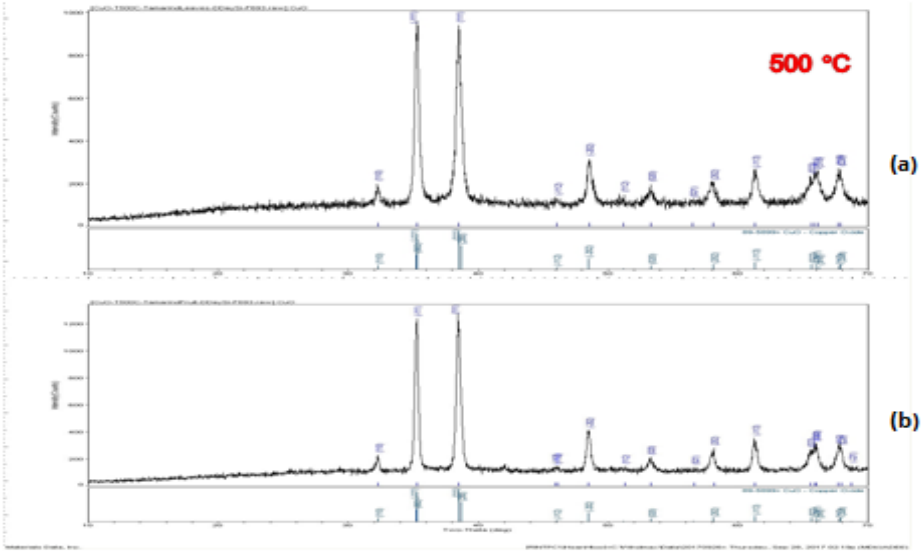


Figure 4 X ray diffractogram of the prepared CuO NPs by using (a) leaves extract and (b) fruits extract of *T. indica* at 500 °C

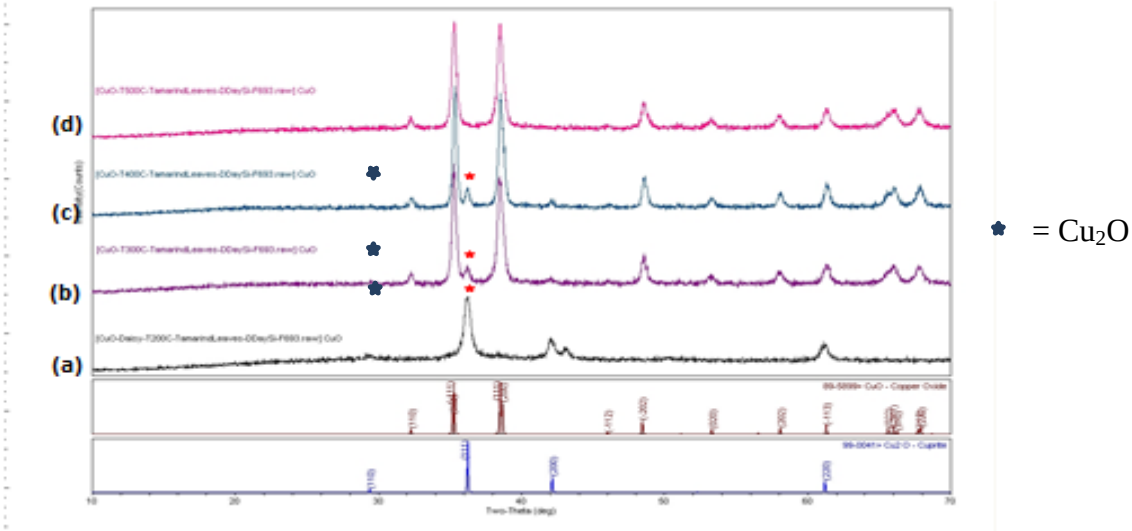


Figure 5 Comparison of X ray diffractograms of the prepared CuO NPs by using leaves extract of *T. indica* at (a) 200 °C (b) 300 °C (c) 400 °C and (d) 500 °C

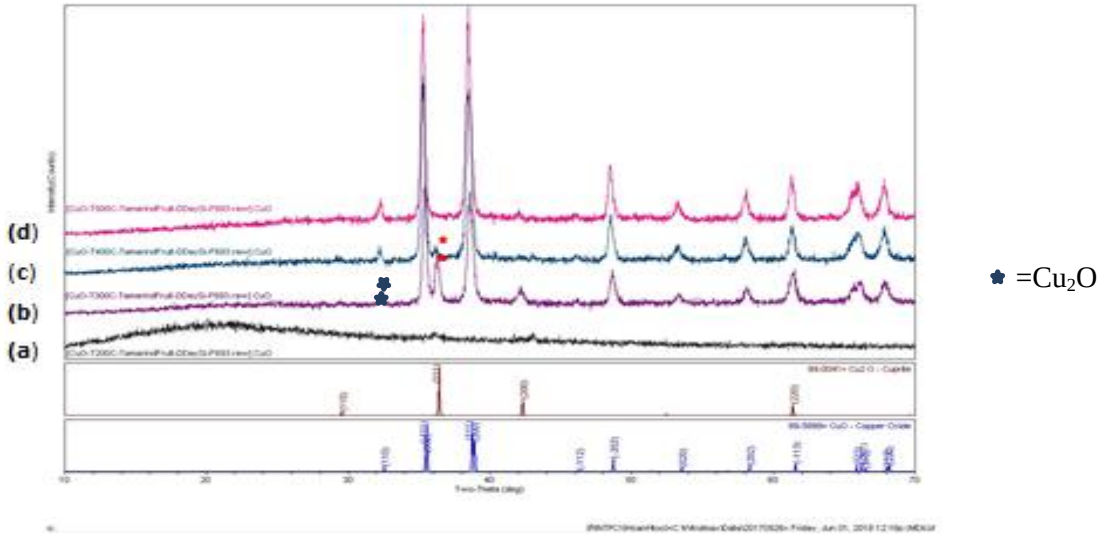


Figure 6 Comparison of the X ray diffractograms of the prepared CuO NPs by using fruits extract of *T. indica* at *(*a) 200 °C (b) 300 °C (c) 400 °C and (d) 500 °C

X –ray analysis is not only used for phase identification but also provide information on crystal structure and unit cell dimension. CuO NPs were indexed as monoclinic with a≠b≠c and $\alpha=\gamma=90^{o}$; $\beta\neq 90^{o}$ (Table 3). From X-ray diffraction analysis, the crystallite sizes of CuO NPs were calculated from full width at half maximum (FWHM) using Scherrer equation according to the following formula:

$$\tau = \frac{0.9\,\lambda}{\beta \cos\theta}$$

where τ is the crystallite size (nm), λ is the diffraction wavelength (0.154056 nm for Cu K α radiation), θ is the diffraction angle (degree) and β is the full width at half maximum (FWHM) for the diffraction peak (radian). The crystallite sizes of CuO NPs using leaves and fruits extracts are shown in Table 4 . As the temperature increased the crystallite sizes were found to decrease, however, the decrease in crystallite size was not pronounced in CuO NPs obtained by using leaves extract of *T. indica*. The crystallite sizes of CuO NPs obtained at 500 ^{o}C were 19.9 nm and 20.9 nm by using leaves extract and fruits extract respectively.

Table 3 Lattice Parameters and Crystal Structures of the Prepared CuO NPs by Using Leaves and Fruits Extracts of *T. indica* at Different Temperatures

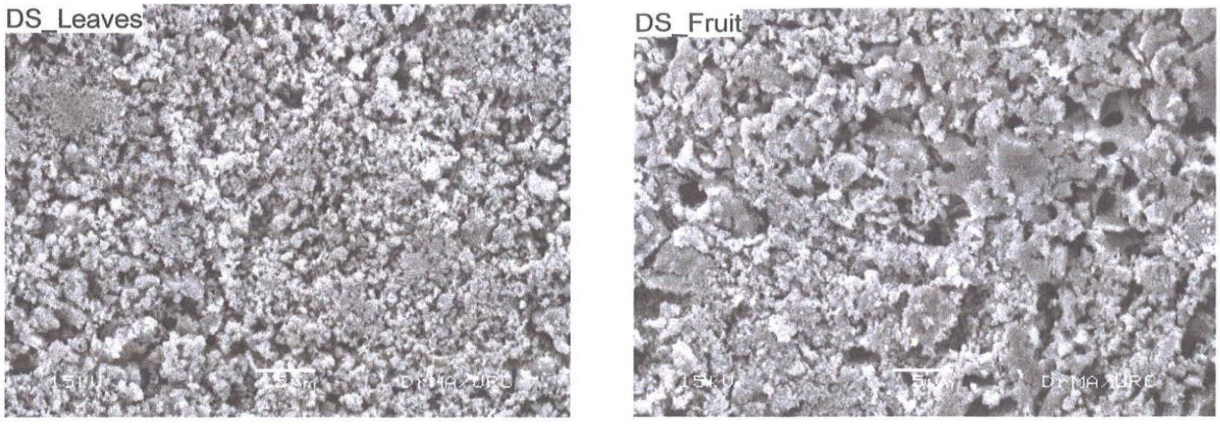
No.	Parameter	Temperature (°C)					
		300		400		500	
		Leaves extract	Fruits extract	Leaves extract	Fruits extract	Leaves Extract	Fruits extract
1	Lattice constant Axial length (Å)	a=4.7235	a=4.6922	a=4.7007	a=4.6984	a=4.7093	a=4.6829
		b=3.4470	b=3.4443	b=3.4536	b=3.4673	b=3.4557	b=3.4614
		c=5.1666	c=5.1573	c=5.1319	c=5.1602	c=5.1307	c=5.1512
2	Interaxial angle (◦)	α,γ=90	α,γ=90	α,γ=90	α,γ=90	α,γ=90	α,γ=90
		β=99.26	β=99.60	β=99.66	β=99.91	β=99.59	β=99.87
3	Crystal structure	Monoclinic		Monoclinic		Monoclinic	

Table 4 Crystallite Sizes of the Prepared CuO NPs at Different Temperatures

No.	Temperature (^{o}C)	Average crystallite size (nm)	
		Leaves extract	Fruits extract
1	300	20.9	26.0
2	400	20.4	21.3
3	500	19.9	20.9

Characterization of the Prepared Copper(II) Oxide Nanoparticles by Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) Analysis

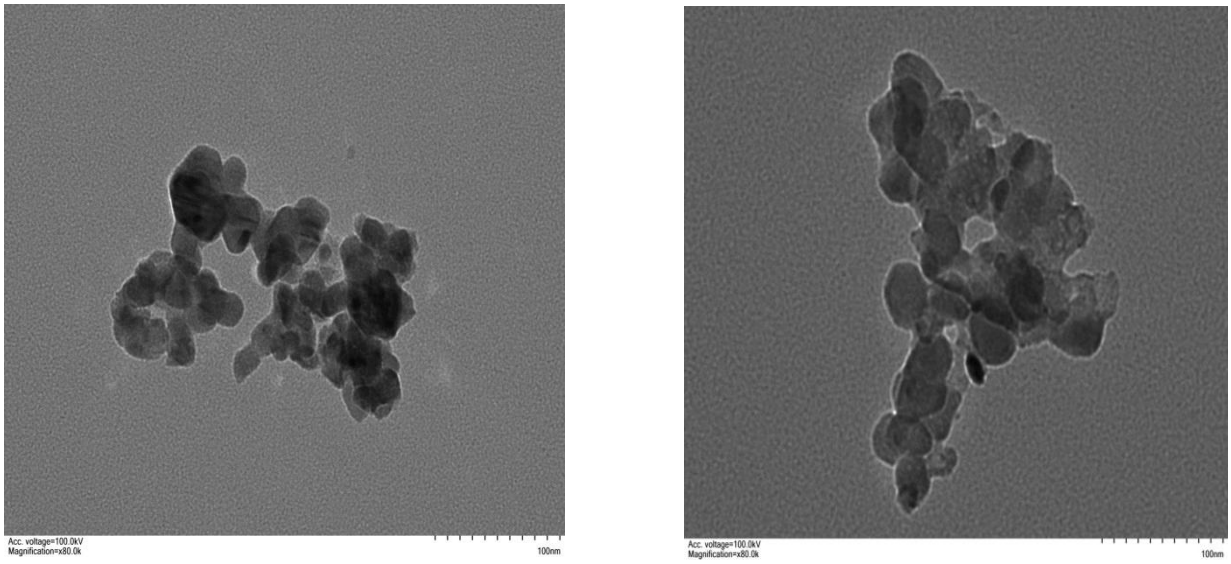
SEM images of prepared CuO nanoparticles by using leaves and fruits extracts are depicted in Figure 7. A large number of quasi-spherical nanoparticles were observed in CuO NPs using leaves extract of *T. indica* and particles with dense agglomerates were observed in those using fruits extract.



(a) (b)

Figure 7 SEM micrographs of the prepared CuO by using (a) leaves extract and (b) fruits extract of *T. indica*

Using TEM analysis, both the size and shape of the obtained nanoparticles were observed. Figure 8 shows TEM images of CuO NPs by using leaves and fruits extracts of *T. indica.* The average sizes of CuO nanoparticles by using leaves and fruits extracts of *T. indica* were found to be 21.2 nm and 21.7 nm respectively. The sizes were not much different from those obtained by X-ray diffraction analysis.



(a) (b)

Figure 8 TEM images of the prepared CuO NPs by using (a) leaves extract and (b) fruits extract of *T. indica* (Magnification=×80.0k)

Characterization of the Prepared Copper(II) Oxide Nanoparticles by Thermogravimetric-Differential Thermal Analysis

Thermal analysis of CuO NPs obtained before calcination was carried out. Figure 9 shows the TG-DTA thermogram of CuO NPs obtained by using leaves extract of *T. indica* and its thermal data are shown in Table 5. Similarly, the thermogram of CuO NPs obtained by using fruits extract and its thermal data are shown in Figure 10 and Table 6. The sfirst endothermic peak was due to the removal of physically sorbed water. The second endothermic peak was due to removal of chemisorbed water. The exothermic peak appeared at 329.43 ºC in CuO NPs by using leaves extract and that appeared at 320.29 ºC in CuO NPs by using fruits extract were due to conversion of Cu_2O to CuO (Xu *et al*., 2004). It was observed that CuO NPs were almost thermally stable beyond 400 ºC. Thus, thermal analysis data confirmed the calcination temperature of 500 ºC for synthesis of CuO.

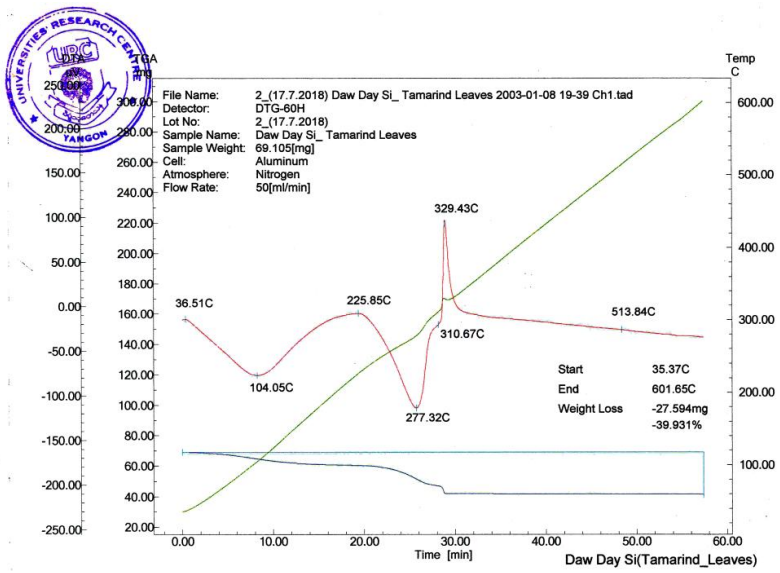


Figure 9 TG-DTA thermogram of the prepared CuO NPs by using leaves extracts of *T. indica*

Table 5 TG-DTA Data of the Prepared CuO NPs by Using Leaves of Extract *T. indica*

No.	Temperature range (°C)	Break in Temp: (°C)	Weight Loss (%)	Nature of Peak	Remark
1	36.51-230	104.05	12.886	Endothermic	Desorption of physically adsorbed water molecules
2	230-310	277.32	19.934	Endothermic	Removal of chemisorbed water
3	310-350	329.43	6.639	Exothermic	Conversion of Cu_2O to CuO
4	350-601.65	-	0.047	-	Thermally stable

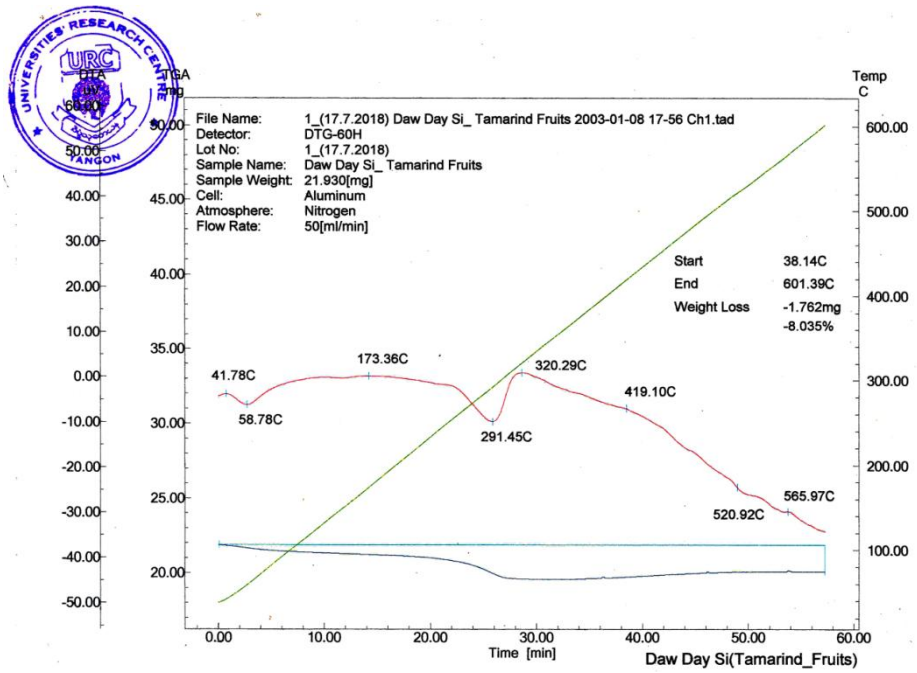


Figure 10 TG-DTA thermogram of the prepared CuO NPs by using fruits extracts of *T. indica*

Table 6 TG-DTA Data of the Prepared CuO NPs by Using Fruits of Extract *T. indica*

No.	Temperature range (ºC)	Break in Temp: (ºC)	Weight Loss (%)	Nature of Peak	Remark
1	41.78-175	58.78	3.556	Endothermic	Desorption of physically adsorbed water molecules
2	175-325	291.45	4.492	Endothermic	Removal of chemisorbed water
3	325-360	320.29	0.008	Small	Conversion of Cu_2O to CuO
4	360-601.39	-	0.002	exothermic	Thermally stable

Characterization of the Synthesized Copper(II) Oxide Nanoparticles by Fourier Transform Infrared Analysis

The synthesized CuO NPs were characterized by FT IR analysis. Figures 11 and 12 show FT IR spectra of CuO NPs. FT IR spectral data are shown in Table 7. The absorption peaks between 430-606 cm^{-1} were attributed to the vibration of Cu-O stretching and indicated the formation of CuO NPs.

Figure 11 FT IR spectrum of the prepared CuO NPs by using leaves extract

Figure 12 FT IR spectrum of the prepared CuO NPs by using fruits extract

Table 7 FT IR Spectral Data of the Prepared CuO NPs by Using Leaves and Fruits Extracts of *T. indica*

No.	Observed Wavenumber (cm^{-1})		Reported value (cm^{-1})	Assignment
	Leaves extract	Fruits extract		
1	511	530	430-606*	Characteristic Cu-O vibration
2	**434**	**461**		

* Alizadeh-Gheshlaghi *et al*., 2012

Conclusion

A simple, eco-friendly and efficient synthesis of CuO NPs by using leaves and fruits extracts of *T. indica* was reported in this study. Aqueous extracts of *T. indica* leaves and fruits have been used as reducing agent and also as a capping agent in the CuO NPs synthesis. The XRD analysis confirmed the crystalline nature of CuO NPs with monoclinic structure and the average crystallite sizes from leaves and fruits extracts were found to be 19.9 nm and 20.9 nm, respectively. Crystallite sizes of CuO nanoparticles from leaves and fruits extracts were 21.2 nm and 21.7 nm by TEM analysis. SEM images showed a large number of quasi-spherical nanoparticles with dense agglomerates. Thermal analysis of CuO nanoparticles showed that CuO was almost thermally stable beyond 400 ºC. The presence of characteristic vibration of Cu-O in the range of 430-606 cm^{-1} was confirmed by FT IR analysis. In future, this green method of synthesizing CuO nanoparticles could also be extended to the fabrication of other industrially important metal oxides.

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