FACILE SYNTHESIS, CHARACTERIZATION AND OPTICAL PROPERTY OF CuO NANOPARTICLES

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Abstract

The synthesis of the cubic-like CuO nanoparticles was achieved by a green method using starch as the capping agent. Starch was extracted from avocado seed, and pH and moisture content of the extracted starch were determined. The extracted starch was then used to prepare CuO- starch composites by using a facile process. The aqueous solutions of 10, 20, and 30 % (w/v) $CuCl_2$ were used not only as a precursor solution for the formation of CuO- starch composites but also as a solvent. The method involves first dissolving the starch in the three different concentrations of $CuCl_2$ aqueous solutions, then adding NaOH to achieve a final pH value of 8.4. When the prepared composites were calcined at 500 °C for 4 h, CuO nanoparticles (CuO NP1, CuO NP2, and CuO NP3) were obtained. The prepared CuO nanoparticles were characterized by different techniques, including XRD, SEM, and FT IR. The average crystallite sizes of CuO nanoparticles were in the range of 33-42 nm. FT IR spectra exhibited only the Cu-O stretching vibrational mode. The CuO nanoparticles were used to investigate the optical property by UV-vis spectrophotometry. According to the UV-Vis spectra of the prepared CuO nanoparticles, the optical band gaps were found to be 3.8 eV for CuO NP1, 3.4 eV for CuO NP2, and 3.3 eV for CuO NP3.

Keywords: avocado seed, CuO-starch composites, CuO nanoparticles, facile synthesis, optical property

Introduction

Nanocrystalline wide-band gap semiconductor particles have drawn considerable interest in recent years due to their interactive properties, such as their large surface-to-volume ratio and distinctive electronic and optical properties as compared to bulk materials (Kidowaki *et al.*, 2012). Moreover, copper oxide nanoparticles have attracted considerable attention due to their unique properties compared to bulk materials. Copper oxide nanoparticles are widely used as gas sensors, catalysts, batteries, high-temperature superconductors, solar energy conversion, surfactants, and antimicrobial and anticancer agents (Alishah *et al.,* 2017). A variety of techniques, including sonochemical, photolytic, chemical reduction, and microemulsion techniques (Hsieh *et al.*, 2003), have been reported for the synthesis of copper oxide nanoparticles. However, the majority of these methods are accompanied by many problems, such as dealing with various toxic and hazardous chemicals. It should be noticed that the development of a green method for the synthesis of copper oxide nanoparticles is an important aspect of current research. That is why, recently, the synthesis of copper oxide nanoparticles using bio-reducing and bio-stabilizing agents produced by different biological systems such as microorganisms, enzymes, and plant or plant extract (Fang *et al.*, 2006) has received increasing attention due to its environmentally benign nature. The ability of plant material to reduce metal ions has been known since the early 1900s. Due to its simplicity, the use of plant materials for reducing metal salts to metal nanoparticles has attracted considerable attention in previous years, and one of these plant materials is starch. The starch has a polymer structure and can cover the surface of the nanoparticles with hydroxyl groups as a capping agent (Cornelia and Christianti, 2017). The main aim of the research is to synthesize CuO nanoparticles by using starch as a capping agent and investigate their structural and optical properties.

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Materials and Methods

Extraction of Starch from Avocado Seed

Firstly, 100 g of avocado seed was cut into small pieces, then 200 mL of distilled water was added and blended by a blender and filtered by a filter cloth, and the filtrate was obtained. The filtrate was dried in an oven at 100 °C for 8 h. It was ground and sieved with a 100 μm sieve. The yield percent of extracted starch was calculated. The pH and moisture content of the extracted starch were determined.

Synthesis of CuO-Starch Composites

In brief, 15 g of the starch extracted from avocado seed was dissolved in 10 %, 20 %, and 30 % (w/v) of $CuCl_2$ aqueous solution while heating at 60 °C with constant stirring. Then a 15 % (w/v) NaOH aqueous solution was added dropwise to the solution, and the solution was stirred with constant stirring to achieve a final pH value of 8.4. After the composites were aged for 30 min with constant stirring at 60 °C, CuO-starch composites were sterilized in an autoclave at 121 °C for 50 min. These were dried in an oven at 80 °C. When it was almost dried, CuO-starch composites were obtained. The composites were characterized by XRD and FT IR for comparison studies.

Preparation of CuO Nanoparticles

The synthesized CuO-starch composites were calcined at 500 °C for 4 h in a muffle furnace. The CuO nanoparticles were washed with distilled water several times to make them free from impurities, and then dried in an oven at 80 °C. The CuO nanoparticles (designated as CuO NP1, CuO NP2, and CuO NP3) were characterized by XRD, SEM, and FT IR.

Optical Properties of CuO Nanoparticles

The optical properties of CuO nanoparticles were studied by UV-vis absorption spectroscopy in the wavelength range of 190-800 nm. The absorption coefficient ($\alpha = 2.303$ (A/t), where A = -log T, T = transmittance and t = thickness of the cell) was calculated from the observed absorption spectra, and the optical band gap of CuO NP1, CuO NP2, and CuO NP3 were calculated from the Tauc's plot of $(\alpha h\nu)^2$ vs $h\nu$ (Tauc *et al.*,1966).

Results and Discussion

Syntheses of CuO-Starch Composites and CuO Nanoparticles

The yield percent of starch extracted from avocado seed was found to be 10.5 %. The pH and moisture content of the extracted starch were observed as 7.17 and 18.25 %, respectively.

The extracted starch was subjected to synthesize CuO-starch composite using 10 %, 20 %, and 30 % $CuCl_2$ solutions giving three CuO-starch composites (composites 1, 2, and 3). By calcination of the composites at 500 °C, three CuO nanoparticles (CuO NP1, CuO NP2, and CuO NP3) were obtained.

XRD Analysis of the Synthesized CuO-Starch Composites and CuO Nanoparticles

X-ray diffraction patterns of CuO-starch composites 1, 2, and 3 are shown in Figures 1 (a), (b), and (c). It was found that all composites show mixed $Cu_2Cl(OH)$ phases and CuO phases. X-ray diffractograms of CuO NP1, CuO NP2, and CuO NP3 are shown in Figures 2 (a), (b), and (c). It was found that XRD patterns show pure CuO peaks.

The average crystallite sizes of samples were calculated from the dominant peaks of X-ray line broadening planes using the Scherrer equation, $D_{Sch} = \frac{0.9\,\lambda}{\beta \cos\theta}$, where D_{Sch} is the average crystallite size, θ is the Bragg angle, λ is the wavelength of the X-ray, β is the full width at half maximum. The average crystallite sizes of the CuO nanoparticles decrease with increase amount of $CuCl_2$ (Tables 1, 2, and 3).

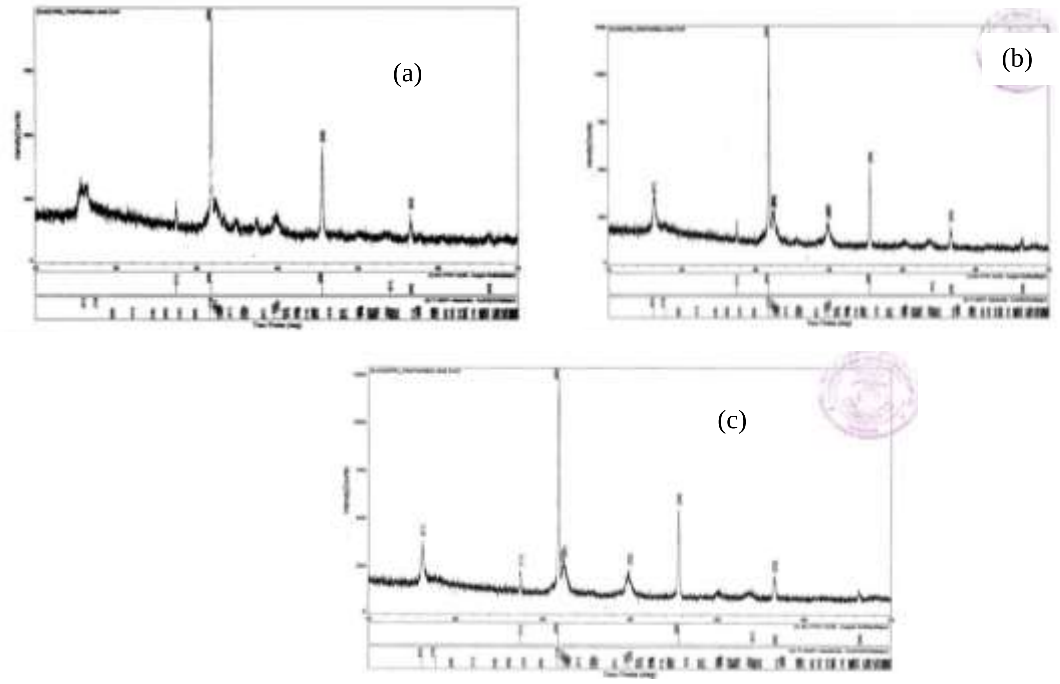

Figure 1. X-ray diffractograms of CuO-starch (a) composite 1, (b) composite 2, and (c) composite 3

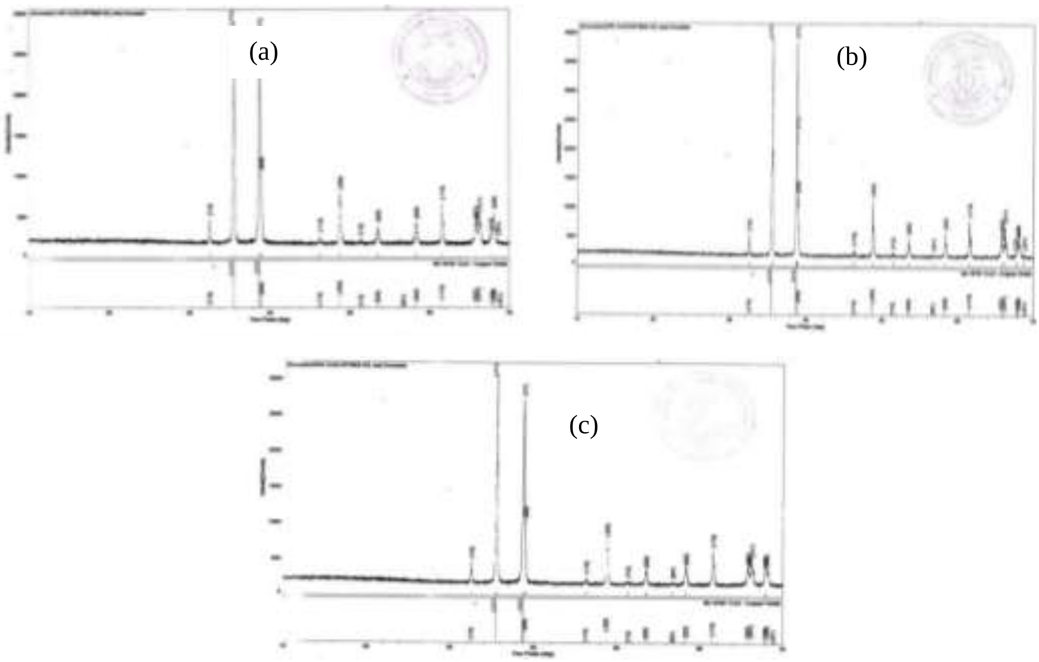

Figure 2. X-ray diffractograms of CuO nanoparticles (a) CuO NP1, (b) CuO NP2, and (c) CuO NP3

Table 1. Average Crystallite Size of the CuO NP1

Sample	2-Theta (degree)	(h k l)	FWHM (degree)	Crystallite size (nm)
CuO NP1	32.503	(1 1 0)	0.172	53.609
	38.727	(1 1 1)	0.170	54.239
	38.892	(2 0 0)	0.356	25.901
	53.459	(0 2 0)	0.219	42.104
	58.317	(2 0 2)	0.195	47.286
	Average crystallite size (nm)			42.489

Table 2. Average Crystallite Size of the CuO NP2

Sample	2-Theta (degree)	(h k l)	FWHM (degree)	Crystallite size (nm)
CuO NP2	32.512	(1 1 0)	0.182	50.663
	38.720	(1 1 1)	0.238	38.742
	38.910	(2 0 0)	0.423	21.798
	53.476	(0 2 0)	0.251	36.736
	58.299	(2 0 2)	0.307	30.035
	Average crystallite size (nm)			34.319

Table 3. Average Crystallite Size of the CuO NP3

Sample	2-Theta (degree)	(h k l)	FWHM (degree)	Crystallite size (nm)
CuO NP3	32.512	(110)	0.179	51.512
	38.729	(111)	0.241	38.260
	38.950	(200)	0.232	39.744
	53.440	(020)	0.329	28.026
	58.260	(202)	0.360	25.613
	Average crystallite size (nm)			33.611

SEM Analysis of CuO Nanoparticles

SEM micrographs of CuO NP1, CuO NP2, and CuO NP3 are shown in Figures 3 (a), (b), and (c). It was found that all samples have agglomerate, porous, and cubic-like crystal structures. CuO NP2 and CuO NP3 particles have more significant crystalline nature than CuO NP1particles. It can be said that CuO NP2 and CuO NP3 particles were formed from the suitable ratios of starting material ($CuCl_2$) and capping agent (starch).

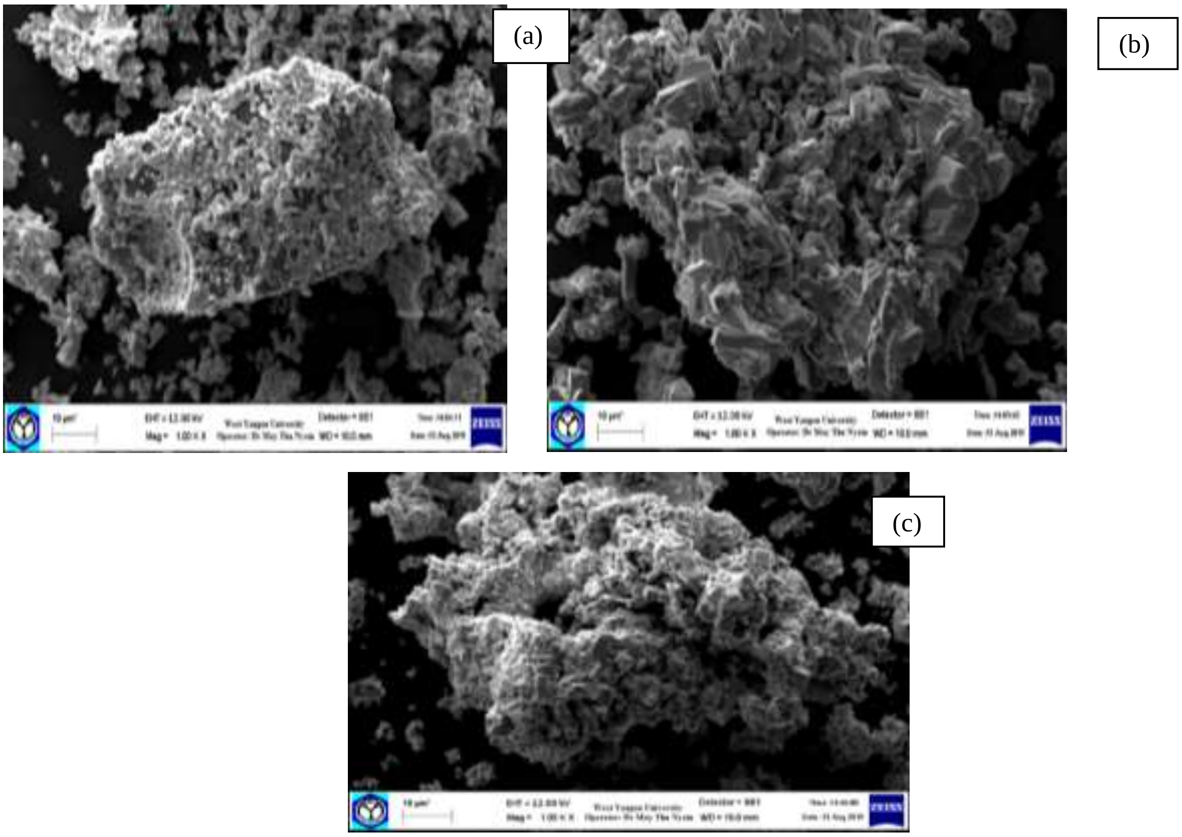

Figure 3. SEM micrographs of CuO nanoparticles (a) CuO NP1, (b) CuO NP2, and (c) CuO NP3

FT IR Analysis of CuO-Starch Composites and CuO Nanoparticles

Figures 4 (a), (b), (c), and Table 4 show the FT IR spectra and assignment data of CuO starch composites 1, 2, and 3.

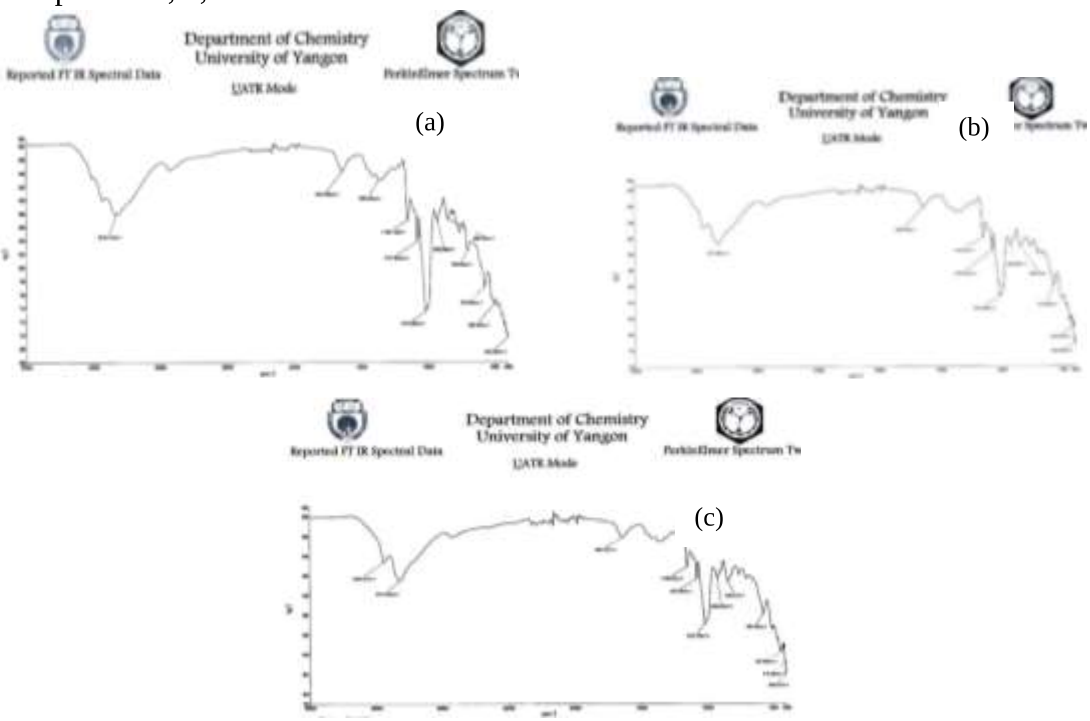

Figure 4. FT IR spectra of CuO-starch (a) composite 1, (b) composite 2, and (c) composite 3

Table 4. FT IR Spectral Data of CuO-Starch Composites

Observed wavenumber (cm^{-1})			*Literature wavenumber (cm^{-1})	Band assignment
Composite 1	Composite 2	Composite 3		
3319	3313	3314	3600-3260	O-H stretching
1634	1640	1637	1630-1690	O-H bending vibration of absorbed water molecules
1150	1150	1150	1149	C-O-C asymmetric stretching
1077 1015	1078 1015	1077 1015	1200-800	C-O stretching
926	923	920	960-910	C-OH deformation
850	844	844	850-790	C-H out of plane bending
573 506 402	572 419 402	572 437 410 402	400-650	Cu-O stretching

***Silverstein *et al.*, 2014

The bands around 3300 cm^{-1} indicate the stretching vibration of the O-H group of CuO-starch composites**.** The bands around 1630 cm^{-1} are assigned to the O-H bending vibration of absorbed water molecules, particularly in the amorphous region of starch (Alemu *et al*., 2022). The peaks around 1150 and 1000-1100 cm^{-1} show the presence of C-O-C asymmetric stretching and C-O stretching vibration, respectively. The band observed around 920 cm^{-1} is assigned to the C-OH deformation of composites. The bands observed around 850 cm^{-1} correspond to C-H out of plane bending of the samples. Cu-O stretching vibration was observed at 400-650 cm^{-1}. Figures 5 (a), (b), (c), and Table 5 show the FT IR spectra and assignment of CuO NP1, CuO NP2, and CuO NP3. All three samples show Cu-O stretching vibration at 400-650 cm^{-1}, which indicates the presence of CuO.

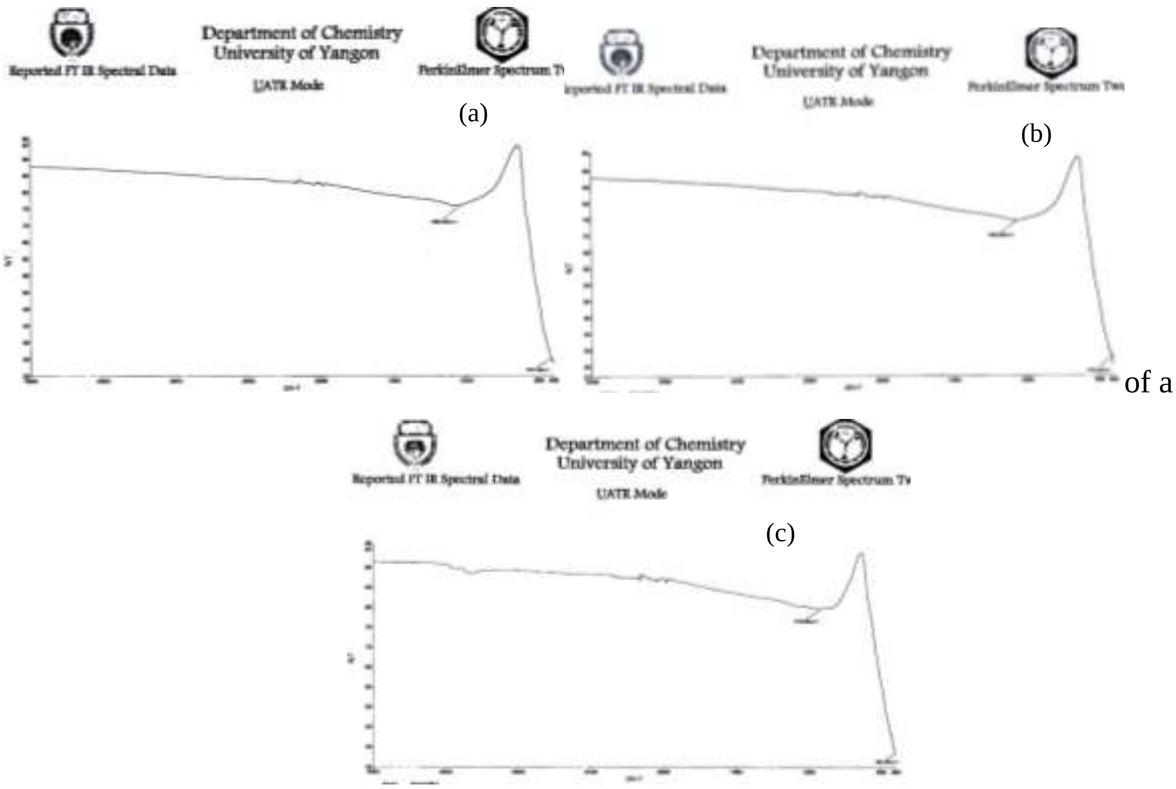

Figure 5. FT IR spectra of CuO nanoparticles (a) CuO NP1, (b) CuO NP2, and (c) CuO NP3

Table 5. FT IR Spectral Data of CuO Nanoparticles

Observed wavenumber (cm^{-1})			*Literature wavenumber (cm^{-1})	Band assignment
CuO NP1	**CuO NP2**	**CuO NP3**		
419	415	403	400-650	Cu-O stretching vibration

*****Silverstein *et al.*, 2014

The Optical Properties of CuO Nanoparticles

The optical properties of CuO nanoparticles (CuO NP1, CuO NP2, and CuO NP3) were studied by UV-Vis absorption spectroscopy in the wavelength range of 190-800 nm. The absorption coefficient (α) was calculated from the observed absorption spectra, and the optical band gaps of CuO nanoparticles were calculated from Tauc's plot of $(\alpha h\nu)^2$ vs hν. Figures 6 (a), (b), and (c) show the optical band gaps of CuO nanoparticles, CuO NP1, CuO NP2, and CuO NP3, which were found to be 3.8 eV, 3.4 eV, and 3.3 eV, respectively. The band gap decreases with an increase in the amount of $CuCl_2$ in the constitutional ratio. According to this band gap, CuO nanoparticles are found within the wide-band gap semiconductor range. Materials can be distinguished by band gap values. Band gap values that lie between 0 and 1 eV are metals, those that lie between 1 and 4 eV are semiconductors, and those that are greater than 4 eV are insulators (Khalaji *et al.*, 2020). Wide-band gap semiconductors permit devices to operate at much higher voltages, frequencies, and temperatures than conventional semiconductors, and they are the key component used to make short-wavelength (green-

UV) LEDs or lasers and are also used in certain radio frequency applications (Yoshikawa *et al.*, 2007).

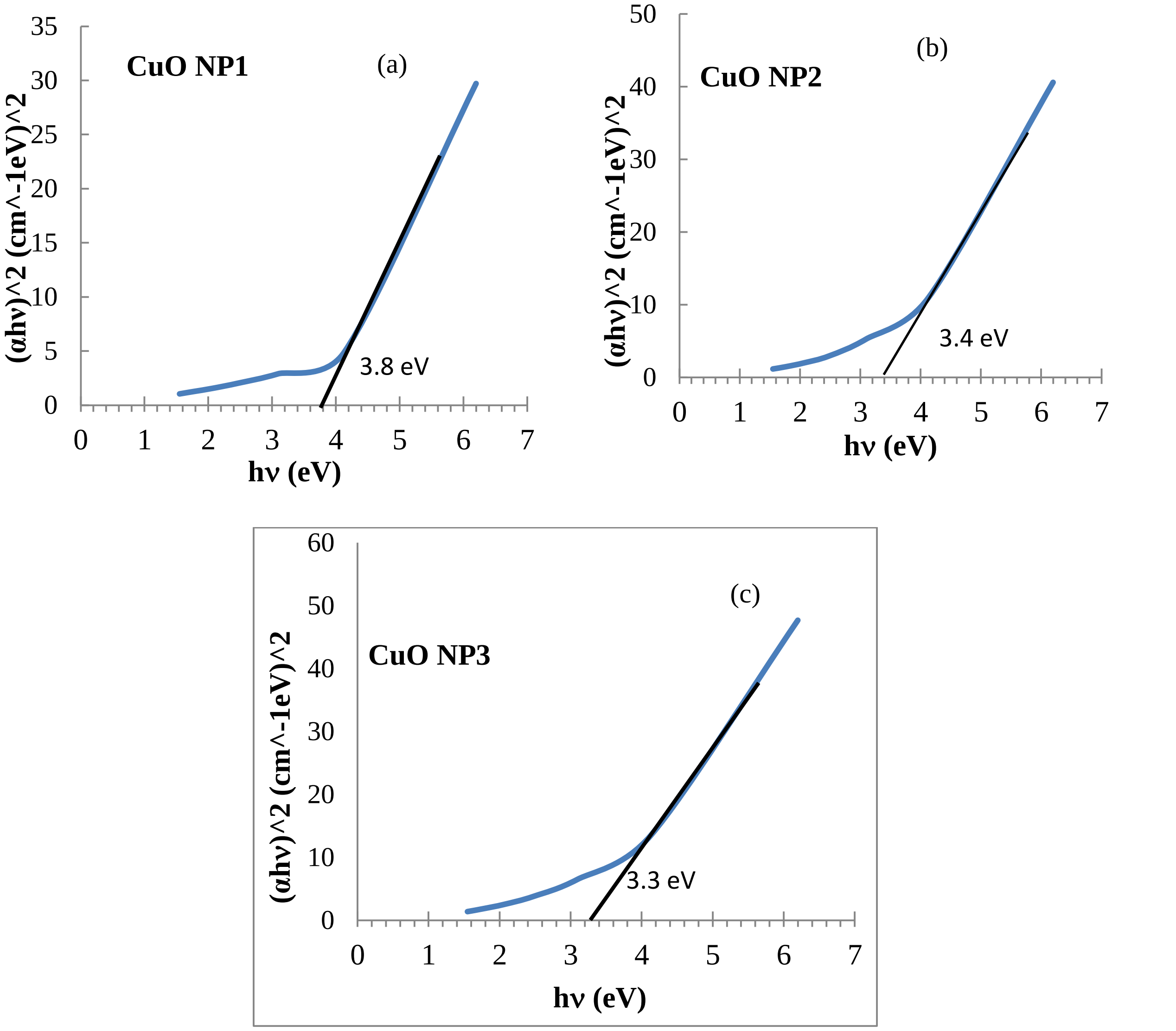

Figure 6. Plot of $(\alpha h\nu)^2$ against h*ν* of (a) CuO NP1, (b) CuO NP2, and (c) CuO NP3

Conclusion

The present study indicates that copper oxide nanoparticles can be prepared by using starch extracted from avocado seed. The method used is low-cost, fast, and simple. From XRD analysis, the average crystallite sizes of CuO NP1, CuO NP2, and CuO NP3 are 42.489 nm, 34.319 nm, and 33.611 nm, respectively. SEM microphotographs of CuO nanoparticles show that all samples have agglomerate, porous, and cubic-like crystalline natures. From FT IR analysis, only the Cu-O stretching vibration band can be observed. The band gap values of CuO nanoparticles indicate a semiconductor band gap range (3.8 eV, 3.4 eV, and 3.3 eV). It can be concluded that the prepared CuO nanoparticles possess wide-band gap values and exhibit good optical properties. Therefore, CuO nanoparticles synthesized by using the avocado seed starch as a capping agent can be used as optical devices, including light- emitting diodes, laser diodes, photodiodes, photoconductive sensors, electro-modulation devices, and optical-optical modulation devices.

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