Asian Journal of Chemistry; Vol. 31, No. 1 (2019), 109-113

ASIAN JOURNAL OF CHEMISTRY

https://doi.org/10.14233/ajchem.2019.21578

A Comparative Study on Copper Oxide Nanoparticles Synthesized from Plant Extracts

A. MUTHUVINOTHINI and S. STELLA*

Department of Chemistry, Sarah Tucker College (Autonomous) (Affiliated to Manonmaniam Sundaranar University), Tirunelveli-627012, India

*Corresponding author: E-mail: stella.selvaraj@gmail.com

Received: 13 July 2018; *Accepted*: 27 August 2018; *Published online*: 30 November 2018; AJC-19167

In the present work, we report the green synthesis of two forms of copper oxide nanoparticles (Cu_2O and CuO) using aqueous extracts of immature coconut fruit and pomegranate peel. The biomolecules present in the plant extract act as reducing and stabilizing agent for the synthesis of nanoparticles. The as-synthesized nanoparticles were characterized using XRD, FT-IR, UV-visible, EDX and SEM analysis. X-ray diffraction analysis confirmed that the synthesized nanoparticle was cuprous oxide (Cu_2O) when aqueous extract of immature *Cocos nucifera* was used as biomaterial whereas cupric oxide (CuO) was formed when aqueous peel extract of *Punica granatum* was used. The size of cuprous oxide nanoparticles was 53 nm and that of cupric oxide nanoparticles was 24 nm. The morphology of the nanoparticles surface was studied by scanning electron microscopy. Further, the formation of CuO/Cu_2O nanoparticles was confirmed by EDX analysis which gives the additional evidence for the formation of copper oxide nanoparticles.

Keywords: Immature coconut fruit, Copper oxide, *Punica granatum*, Peel extract, Cuprous oxide, Nanoparticles.

INTRODUCTION

Nanoparticles are widely used in many fields because of its size and tunable properties [1-3]. Synthesis of nanoparticles by using biological methods is important because biological methods are safe, low cost, environment friendly and can be used in large scale synthesis as an alternative to chemical and physical methods [4-6]. Recent reports of plant extract for the production of nanoparticles have shown that broad range of biomolecules such as alkaloids, terpenoids, phenols, flavonoids, tannins, quinines *etc*. are known to mediate synthesis of nanoparticles [7].

Among all the nanoparticles, copper oxide (CuO) nanoparticles find wide applications in agricultural, industrial engineering and technological fields [8,9]. Lee *et al*. [10] have reported the synthesis of copper nanoparticles from the leaf extract of *Magnolia kobus*. Kolekari *et al*. [11] prepared copper nanoparticles using Eucalyptus leaf extract. Singh *et al*. [12] reviewed the syntheses of copper nanoparticles using different plant extracts. In the present study, it is proposed to synthesize copper oxide nanoparticles by using the biowaste *viz*. immature fruit of *Cocos nucifera* (Coconut tree) and the peel of *Punica granatum* (pomegranate). The biowaste such as peel of pomegranate and the immature coconut fruit fallen from the coconut tree was used for the preparation of copper oxide nanoparticles, thereby a waste material was used to produce a worthy product. This is the first time that the synthesis of nanoparticles using immature coconut fruit is demonstrated.

Kaur *et al*. [13] synthesized copper nanoparticles using methanolic extract of pomegranate peel and studied the antimicrobial activity of synthesized nanoparticle. Herein, we report a simple method for the synthesis of CuO nanoparticle from the aqueous peel extract of *Punica granatum*. On comparing to the reported work for the preparation of copper nanoparticles, our method is simple and the synthesis of nanoparticles was carried out at room temperature. The CuO nanoparticles were formed instantly upon the addition of copper sulphate aqueous solution to the aqueous peel extract of pomegranate.The synthesized nanoparticles were characterized with the spectroscopic methods such as UV-visible, FT-IR, SEM, EDX and XRD analyses. The phytochemical analysis of immature coconut fruit and *Punica granatum* peel was done to identify the bioconstituents responsible for the reduction of metal salt.

EXPERIMENTAL

The fresh immature coconut fruit which was fallen from the coconut tree was collected from Tirunelveli area, India. Pomegranate fruit was purchased from the local market of Tirunelveli city of India. Copper sulphate pentahydrate and sodium hydroxide were purchased from Nice chemicals, India. All the aqueous solutions were prepared with double distilled water.

Preparation of pomegranate peel extract: The fresh peel of pomegranate was ground with mortar and pestle, and then dispensed in 100 mL of distilled water. The extract was then filtered and this filtrate was collected in a clean and dried beaker. The fresh extract is used for the preparation of CuO nanoparticles.

Preparation of immature coconut fruit extract: Initially, the fixative of the immature coconut fruit was removed off. The immature fruit was cut into small pieces with ethanol sterilized knife and grounded with a mortar and pestle. Then, the slurry was dispensed in 100 mL of distilled water. The extract was filtered using Whatmann No.1 filter paper.

Synthesis of copper oxide (CuO/Cu_2O) nanoparticles: About 100 mL of immature coconut fruit extract/pomegranate peel extract was mixed with 100 mL of 0.1M $CuSO_4·5H_2O$ solution, when the two solutions were mixed, colour of the solution became green. When 5 mL of 0.1 M NaOH solution was added to the above solution, brown colour precipitate of copper oxide nanoparticles slowly started to settle down. The precipitate was filtered and dried at 100 ºC for 2 h in a hot air oven in the case of nanoparticles prepared from immature fruit extract of *Cocos nucifera* and the precipitate formed from the *Punica granatum* peel extract was filtered, washed and dried at 500 ºC for 5 h in a muffle furnace.

Detection method: Optical absorption spectra of the synthesized nanoparticles were taken in the UV-visible double beam spectrophotometer 2201, Systronics using a quartz cuvette of 1 cm path length. FT-IR spectra of the nanoparticles were recorded at room temperature on IR affinity (FT-IR spectrophotometer, Shimadzu) ranging from 4000 to 400 cm^{-1}. The morphology of the synthesized nanoparticle is studied by scanning electron microscopy (JEOL). The synthesized CuO nanoparticle was analyzed by powder X-Ray diffraction technique using X-Ray Diffractometer (Shimadzu) with $CuK_{\alpha1}$ radiation (k = 1.54 Å) in the 2θ range of 10º-80º. The elemental composition and stoichiometry of the synthesized nanoparticles was studied by EDAX instrument (Oxford Instruments).

RESULTS AND DISCUSSION

Phytochemical analysis of plant extracts: The presence (+) and absence (-) of phytochemical compounds in the aqueous immature fruit extract of *Cocos nucifera* and the aqueous peel extract of *Punica granatum* was analyzed by using different experimental methods and the results are tabulated in Table-1.

Synthesis of copper oxide nanoparticles: The amount of plant extract and the metal salt solution needed to synthesize the nanoparticles were optimized by adding various amount of extract to $CuSO_4$ solution. After the elaborate process of optimization, it was found that equal amount of extract and 0.1M $CuSO_4$ solution was ideal to prepare CuO/Cu_2O nanoparticles. The CuO/Cu_2O nanoparticles were prepared by mixing 100 mL of plant extract with 100 mL of 0.1M $CuSO_4$ solution. The reducing agents present in the extract were responsible for the formation of copper oxide nanoparticles. When the extract (brown in colour) was mixed with $CuSO_4$ solution (blue in colour), the resulting solution became green. Then 5 mL of 1 M NaOH solution was added to the above solution as the precipitating agent, Cu_2O/CuO nanoparticles started to precipitate slowly and it was filtered and dried. The constituents in the extracts itself act as a reducing and capping agent to prevent the agglomeration of nanoparticles.

TABLE-1
PHYTOCHEMICAL ANALYSIS OF IMMATURE COCONUT FRUIT EXTRACT AND POMEGRANATE PEEL EXTRACT

Phytochemical compounds	Immature fruit extract of *Cocos nucifera*	Peel extract of *Punica granatum*
Steroids	+	+
Reducing sugars	+	+
Carbohydrate	+	+
Alkaloids	+	+
Phenolic compounds	+	+
Saponins	+	–
Xanthoproteins	–	–
Terpenoids	+	–
Flavonoids	+	–
Coumarins	–	–

X-ray diffraction analysis of CuO nanoparticles: Powder diffraction analysis indicated that the product synthesized from immature coconut fruit extract was cuprous oxide nanoparticles (Cu_2O nanoparticles) (Fig. 1a) and copper oxide nanoparticles in case of *Punica granatum* peel extract (Fig. 1b). The diffraction peaks observed at 2θ values of 38.2º, 44.3º, 77.8º are indexed to (111), (200) and (222) planes of cuprous oxide nanoparticles (Fig. 1a) and compared with the single phase cubic structure (JCPDS file no. 05-0667). The XRD study confirms that the resultant particles are Cu_2O nanoparticles.

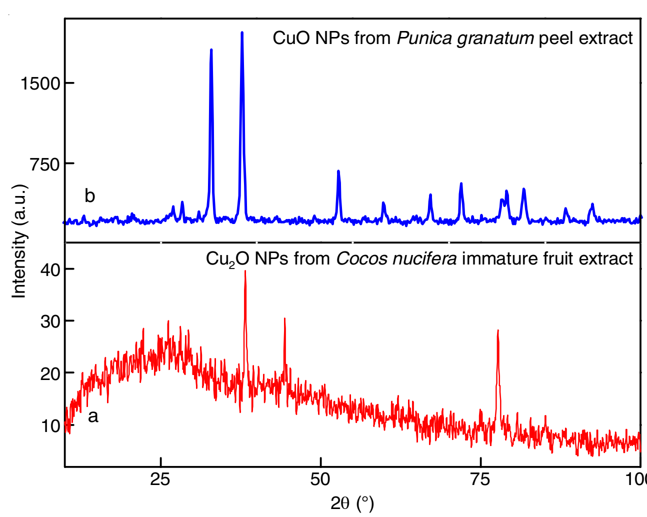

Fig. 1. XRD Pattern of CuO/Cu_2O nanoparticles

The diffraction patterns observed at 2θ values of 35.2º, 38.4º, 48.4º for the copper oxide nanoparticles in Fig. 1b are identical to the single phase monoclinic (JCPDS: 80-1916) structure. The sharp peaks of XRD indicated that the synthesized nanoparticles are highly crystalline in nature. The average particle size of copper oxide and cuprous oxide nanoparticle has been estimated by using Debye-Scherrer formula [$D = K\lambda/\beta\cos\theta$]. The average diameter of the particle was found to be about 24 nm for CuO and about 53 nm for Cu_2O nanoparticles.

UV-visible spectrum of CuO/Cu_2O nanoparticles: The UV-visible spectrum of CuO nanoparticles solution is shown in Fig. 2. When the pomegranate peel extract was mixed with $CuSO_4$, the UV-visible spectrum was broad with a band at 206 nm (CuO nanoparticles) and two small humps are shown in 246 and 283 nm which are due to the presence of phytoconstituents in the aqueous peel extract [14] (Fig. 2a), but after the addition of NaOH, the concentration of nanoparticles was increased as evidenced by a sharp peak at 216 nm (Fig. 2b). This peak can be assigned to the absorption of mono dispersed copper oxide nanoparticles [15].

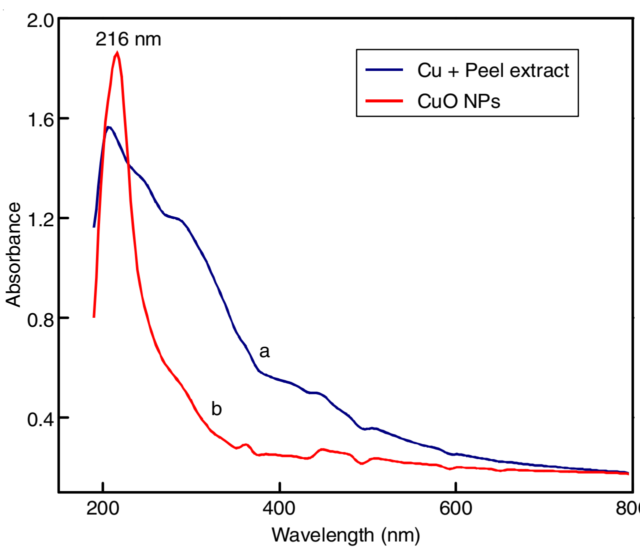

Fig. 2. UV-visible spectra of (a) mixture of extract and $CuSO_4$ solution (green color); (b) Colloidal CuO nanoparticles solution after the addition of base

Fig. 3 represents the UV-visible absorption spectra of immature coconut fruit extract (Fig. 3a), extract and copper sulphate mixture (Fig. 3c), cuprous oxide nanoparticles (Fig. 3b), respectively. Cuprous oxide nanoparticles typically exhibit absorption peak around 400-600 nm [16]. However, the cuprous oxide nanoparticles synthesized from immature coconut fruit extract show one absorption peak and two more humps around in the range of 398-569 nm. The band at avout 410 nm is mainly due to cuprous oxide nanoparticle and the two more small bands are due to phytoconstituents which are attached to Cu_2O nanoparticle surface (Fig. 3b). The reduction of $CuSO_4$ occurred due to the water-soluble phytochemicals present in the extract.

FT-IR analysis of CuO nanoparticles: In order to understand the nature of capping agent and the presence of different functional groups responsible for the synthesis of mono dispersed CuO/Cu_2O nanoparticles, FT-IR analysis was carried out. The FT-IR spectrum of Cu_2O nanoparticles Fig. 4a shows the characteristic absorption bands at 3387, 1605, 1103 cm^{-1} corresponds to H-O-H stretching, H -bonded alcohols and phenols, C-H alkyl stretching, which confirm the presence of phyto-constituents such as polyphenols, alkaloids, steroids in the nanoparticles surfacewhich may act as the capping agent. The peaks at 470.63 cm^{-1} (Cu-O sym. *str.*) and 601.79 cm^{-1} (Cu-O wagging) imply the presence of metal-oxide group in the sample [17].

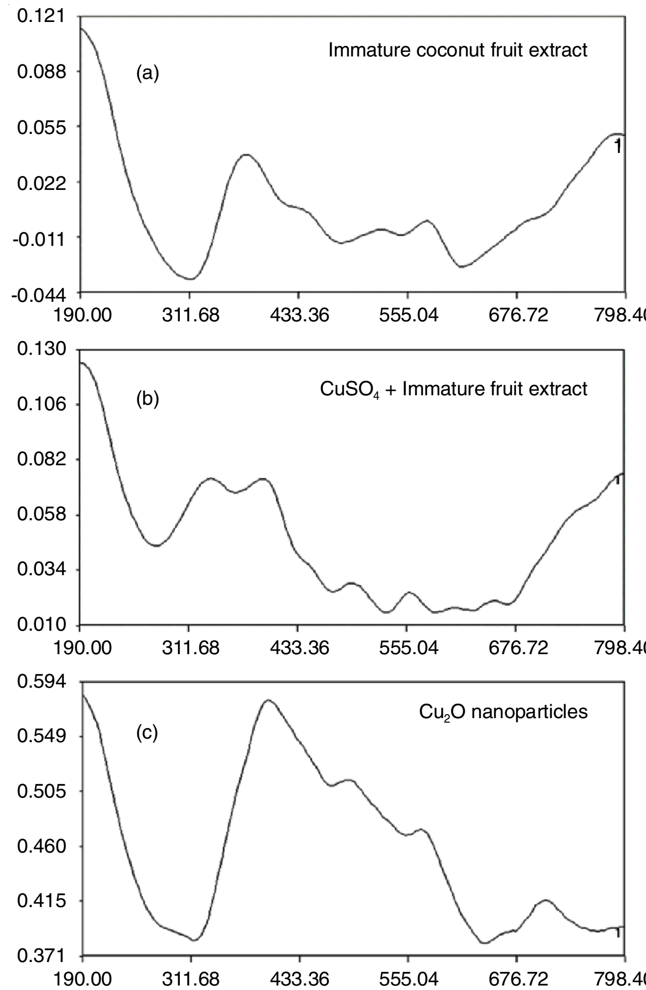

Fig. 3. UV-visible spectra of (a) immature coconut fruit extract (b) copper sulphate + immature coconut fruit extract (c) cuprous oxide nanoparticles

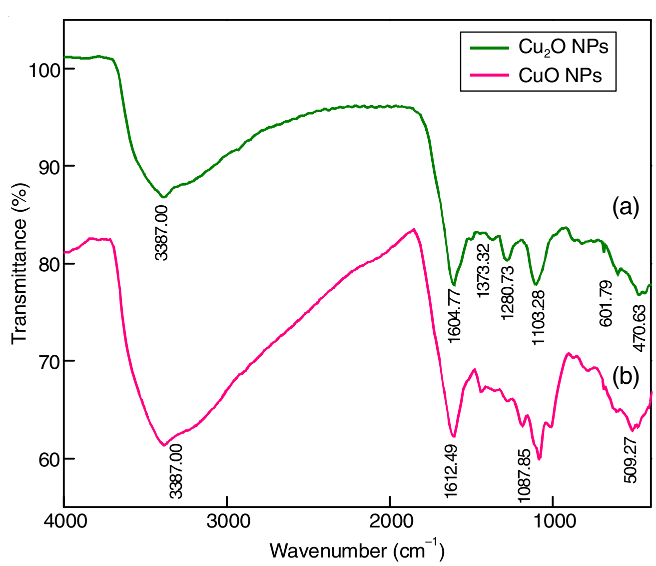

Fig. 4. FT-IR spectrum of (a) Cu_2O nanoparticles from immature fruit extract of *Cocos nucifera* (b) CuO nanoparticles from *Punica granatum* peel extract

The FT-IR spectrum of copper oxide nanoparticles is shown in Fig. 4b. The FT-IR spectrum of CuO nanoparticles (Fig. 4b) shows the characteristic absorption bands at 3387, 1612, 1087 and 509 cm^{-1} corresponds to H-O-H stretching, H-bonded alcohols and phenols, C-H alkyl stretching, C-H stretching which confirm the presence of phytoconstituents such as polyphenols, alkaloids, steroids and reducing sugars in the nanoparticles surface that may act as the capping agent. The peaks at 478 cm^{-1} (Cu-O sym. *str*.) and 609.51 cm^{-1} (Cu-O wagging) imply the presence of metal-oxide group in the sample. The metal-oxygen bond is observed at 1350 cm^{-1} (M-O rocking in plane) indicates the formation of CuO from copper sulphate [17]. Peaks at 1010 and 784 cm^{-1} are due to the interaction of CuO nanoparticle and extract of pomegranate peel [18].

SEM analysis of CuO/Cu_2O nanoparticles: The morphology of prepared CuO and Cu_2O nanoparticles was examined by scanning electron microscopy (SEM). Fig. 5a and 5b depict the SEM images of CuO nanoparticles synthesized from *Punica granatum* peel extract at different magnifications. The synthesized copper oxide nanoparticles have an irregular planar structure with no distinct morphology. Similarly, Fig. 6a-b depicts the SEM images of cuprous oxide nanoparticles synthesized from immature fruit extract of *Cocos nucifera*. It shows that the cuprous oxide nanoparticles are relatively in uniform spherical shape.

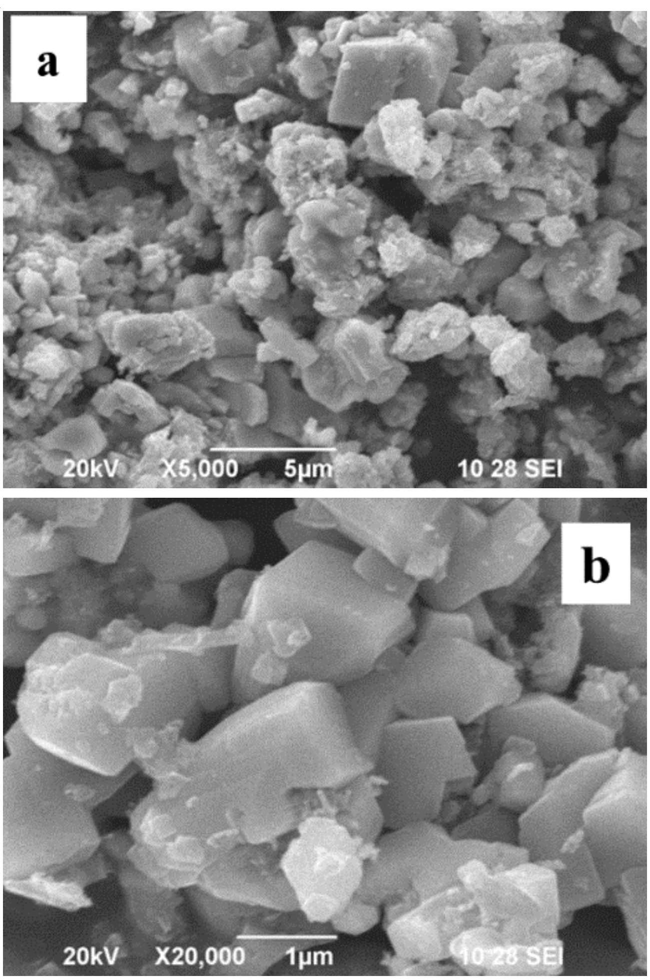

Fig. 5. SEM images of CuO nanoparticles synthesized from pomegranate peel extract at different magnifications (a) 5 μm (b) 1 μm

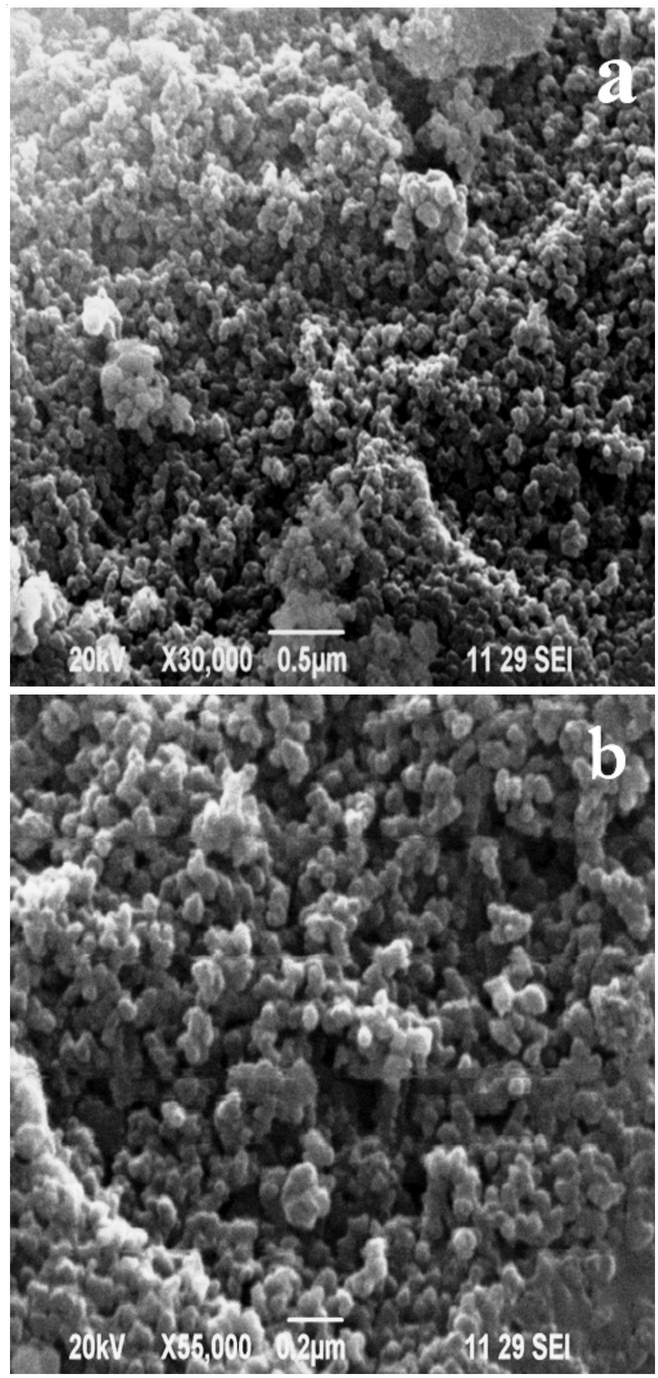

Fig. 6. SEM images of Cu_2O nanoparticles synthesized from immature coconut fruit extract at different magnifications (a) 0.5 μm (b) 0.2 μm

Energy dispersive spectroscopic analysis: Energy dispersive X-ray (EDX) analysis was carried out to determine the elemental composition and stoichiometry of the synthesized nanoparticles. Energy dispersive X-ray analysis gives the additional evidence for the formation of CuO/Cu_2O nanoparticles by the biosynthesis. Comparing the two EDX spectra (Fig. 7), it was found that Cu signals are different in each spectrum which further confirmed the formation of cupric oxide and cuprous oxide nanoparticles. The spectrum for CuO nanoparticles shows copper and oxygen signals along with potassium and sulphur peaks, which may be originating from the biomolecules that are bound to the surface of CuO nanoparticles.

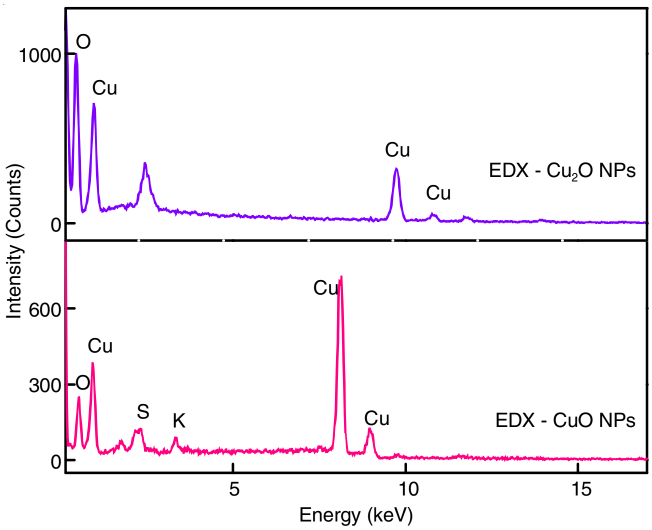

Fig. 7. Energy dispersive X-ray spectrum of synthesized Cu_2O nanoparticles

Conclusion

In summary, green syntheses of CuO/Cu_2O nanoparticles from immature fruit of *Cocos nucifera* (Coconut tree) and the peel of *Punica granatum* (pomegranate) are demonstrated. The biomolecules like alkaloids, steroids, carbohydrates and phenolic compounds present in the extracts are responsible for the reduction of copper sulphate to copper oxide nanoparticles. The formation of CuO/Cu_2O nanoparticles was confirmed by UV-visible, IR and XRD analyses. The morphology of the nanoparticle surface was studied by scanning electron microscopy and EDX analysis gives the additional evidence for the formation of CuO/Cu_2O nanoparticles.

ACKNOWLEDGEMENTS

The authors are grateful to DST-SERB (ECR/2016/001523), India for the financial assistance.

CONFLICT OF INTEREST

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

REFERENCES

1. S. Bagherim, I.S. Amiri, A.T. Youseli and S.B.A. Hamid, Nanocomposites in Electrochemical Sensors, CRC Press: London (2017).
2. P. Khandel and S.K. Shahi, *Int. J. Nanomater. Bio. Struct.*, **6**, 1 (2016).
3. J.C. Tarafdar, S. Sharma and R. Raliya, *Afr. J. Biotechnol.*, **12**, 219 (2013); https://doi.org/10.5897/AJB12.2481.
4. E.A. Mergani and A.A. Ibrahim, *Int. J. Recent Sci. Res.*, **7**, 8766 (2016).
5. B.H.M. Piramila, A.L. Prabha and V. Nandagopalan, *Int. J. Pharm. Res. Scholars*, **3**, 809 (2014).
6. G. Deepika and C. Pratima, *J. Nanomed. Res.*, **5**, 00110 (2017); https://doi.org/10.15406/jnmr.2017.05.00110.
7. The Minerals, Metals and Materials Society, 144th Annual Meeting & Exhibition (TMS 2015), Annual Meeting Supplemental Proceedings, Springer, p. 123 (2016).
8. G. Shobha, M. Vinutha and S. Ananda, *Int. J. Pharm. Sci. Invent.*, **3**, 28 (2014).
9. A.B. Seabra and N. Durán, *Metals*, **5**, 934 (2015); https://doi.org/10.3390/met5020934.
10. H.J. Lee, G. Lee, N.R. Jang, J.H. Yun, J.Y. Song and B.S. Kim, *NSTI-Nanotechnol.*, **1**, 371 (2011).
11. R.V. Kolekari, S.P.D. Bhade, R. Kumar, R. Priyanka, R. Singh and K.S. Pradeepkumar, *Curr. Sci.*, **109**, 2149 (2015).
12. J. Singh, G. Kaur and M. Rawat, *J. Bioelectron. Nanotechnol.*, **1**, 01 (2016).
13. P. Kaur, R. Thakur and A. Chaudhury, *Green Chem. Lett. Rev.*, **9**, 33 (2016); https://doi.org/10.1080/17518253.2016.1141238.
14. M. Shanmugavadivu, S. Kuppusamy and R. Ranjithkumar, *Am. J. Adv. Drug Deliv.*, **2**, 174 (2014).
15. R. Mittu, *Int. Adv. Res. J. Sci. Eng. Technol.*, **3**, 37 (2016);
16. M.L. Bhaisare, M.S. Khan, S. Pandey, G. Gedda and H.-F. Wu, *RSC Adv.*, **7**, 23607 (2017); https://doi.org/10.1039/C6RA28705K.
17. I.Z. Luna, L.N. Hilary, A.M. Sarwaruddin Chowdhury, M.A. Gafur, N. Khan, R.A. Khan, *Open Access Lib. J.*, **2**, 1 (2015); https://doi.org/10.4236/oalib.1101409.
18. P. Huang, Z. Li, H. Hu and D. Cui, *J. Nanomater.*, **Article ID**, 641545 (2010); https://doi.org/10.1155/2010/641545.