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Green Synthesis, Structural and Optical Properties of Copper Oxide Nanoparticles using Malva Parviflora

*Wedad M. Barag, Fatma A. Shtewi, and Awatif A. Tarroush

Chemistry Department, Faculty of Science, Azawia University, Libya

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ABSTRACT

Green Synthesis of cupric Oxide nanoparticles (CuONPs) using the plant extract is an emerging field of extensive applications. In the present study, the CuONPs were carried out by reducing copper sulfate solution by the aqueous Malva parviflora leaves extract, where this plant is used as a reducing and capping agent. The precursor salt solution and reducing agent were mixed in a 1:4 volume ratio at 50 oC and pH=9. According to the UV-VIS spectrum, the surface plasmon resonance (SPR) absorption band was observed at 262 nm. UV-VIS spectroscopy also was employed to estimate the band gap energy of CuO nanoparticles, in which the optical band gap was varied depending upon the particle size and copper sulfate concentration. The XRD was found that synthesized CuONPs were Amorphous structure. FT-IR spectrum revealed that the presence of flavonoid may be the significant cause of reducing and capping of CuONPs. Furthermore, the mechanism of CuO nanoparticle formation has also been discussed.

الاصطناع الأخضر، الخواص التركيبية والضوئية لجسيمات اوكسيد النحاس النانوية باستخدام نبات الخبيزة

*وداد محمد برق و فاطمة علي الشتيوي و عواطف عبد السلام طروش

قسم الكيمياء،كلية العلوم،جامعة الزاوية،ليبيا

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الملخص

يعد الاصطناع الأخضر للجسيمات النانوية لأكسيد النحاسيك (CuONPs) باستخدام المستخلص النباتي مجالًا ناشئًا لتطبيقات واسعة النطاق. في هذه الدراسة ، تم إصطناع الجسيمات النانوية CuO عن طريق اختزال محلول كبريتات النحاس بواسطة المستخلص المائي لاوراق الخبيزة. تم خلط محلول الملح البادئ وعامل الاختزال بنسبة حجمية 1: 4 عند 50 درجة مئوية ودرجة حموضة pH=9. وفقًا لطيف الأشعة المرئية وفوق البنفسجية ، لوحظ أن نطاق امتصاص رنين البلازمون السطحي (SPR) عند 262 نانومتر. تم أيضًا استخدام التحليل الطيفي للأشعة المرئية وفوق البنفسجية لتقدير طاقة فجوة النطاق لجسيمات اوكسيد النحاسيك النانوية ، حيث تباينت فجوة النطاق البصري اعتمادًا على حجم الجسيمات وتركيز كبريتات النحاس. اشعة الحيود السينية بينت ان الشكل غير متبلور. أظهر طيف الاشعة تحت الحمراء ان الفلافونيد سبب مهم لاختزال واستقرار الجسيمات النانوية لاوكسيد النحاسيك. علاوة على ذلك ، تمت أيضًا مناقشة آلية تكوين الجسيمات النانوية لاوكسيد النحاسيك.

1. Introduction

copper oxide nanoparticles (CuONPs) based semiconducting materials have recently gained renewed interest for potential applications in lithium-ion electrode materials [1], sensors [2, 3], photovoltaic devices [4] catalysis [5,6], and biomedicine [7], due to it possess unique optical and catalytic and electric properties differing from the bulk. It is an attractive p-type metal oxide semiconductor with an indirect band gap of 1.21-2.51 eV and a monoclinic crystal structure [8]. It has a high dielectric constant semiconductor. Thermodynamically, the CuO phases are more stable than pure copper [9].

Various physical and chemical methods like sol-gel, co-precipitation, laser ablation, Sonochemical, and Solid-State methods have been

*Corresponding author:
E-mail addresses: w.barag@zu.edu.ly, (F. A. Shtewi) f.shtewi@zu.edu.ly, (A. A. Tarroush) a.tarroush@zu.edu.ly
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reported for the synthesis of CuONPs with desired morphologies qualities [10]. However, these methods involve the hazardous chemicals, very expensive, and non-environmentally friendly chemicals [11]. Recently, green synthesis using plant (Biosynthesis) is a non-toxic, cost-effective, eco-friendly, and valuable alternative for the large-scale production of metal nanoparticles [12]. The advantages of using plant and plant-derived materials for biosynthesis of metal nanoparticles have interested researchers to investigate mechanisms of metal ions uptake and bioreduction by plants and to understand the possible mechanism of metal nanoparticle formation in plants [13].

Malva parviflora Linn., a member of the family *Malvaceae*, also commonly known as cheese weed, has been reported as an antioxidant [14], antidiabetic, antifungal [15]. In Libya, Malva parviflora leaves have been used as food where it was cooked as a soup or a stew and served with bread. The aqueous Malva parviflora leaves extract contains polyphenol, flavonoid, tannin, alkaloid, resin, and saponins [14]. Shehata and Galal reported that the Malva parviflora leaves had the highest value of flavonoids was approximately about 32.02 mg/g [16]. In addition, Al-Qarawi and Al-Obaidi reported that the major bioactive compound in Malva parviflora leaves extract is rutin [17]. The high rutin content of the aqueous Malva parviflora leaves extract having strong antioxidant properties helped in the reduction of copper (II) ions to CuO nanoparticles. According to the authors' knowledge, it is the first time to use aqueous Malva parviflora leaves extract for the synthesis of CuO nanoparticles. In our study, we report the green synthesis of Cupric oxide nanoparticles (CuONPs) via a single-step reduction of copper ions using aqueous Malva parviflora leaves extract as a reducing agent at a low temperature about 50 ^{0}C [18]. Copper sulfate, aqueous Malva parviflora leaf extract, and sodium hydroxide were used as starting materials. The synthesized CuO nanoparticles were characterized by UV-VIS, XRD and FT-IR.

2. Materials And Methods

Fresh leaves of *Malva parviflora* plant were collected from Az-Zāwiyah, Libya. Copper sulfate pentahydrate ($CuSO_4.5H_2O$) and Sodium hydroxide (NaOH) were purchased from Sigma Aldrich.

2.1 Aqueous Malva parviflora Leaves Extract Preparation

The fresh Malva Parviflora leaves were collected from Az-Zāwiyah, Libya. The leaves were thoroughly washed several times using normal water and then followed by distilled water to remove impurities. The (10 g) of leaves were cut and boiled with 100 ml of distilled water for 15 min. then it was cooled down to room temperature. The prepared solution was initially filtered through Whatman No.1 filter paper. The filtrate was stored at 4°C for future works [19].

2.2 Cupric Oxide Nanoparticles Preparation

CuO nanoparticles were synthesized by adding freshly prepared leaves extract to $CuSO_4$ solution (0.1 M) in a 1:4 volume ratio. The solution was mixed well followed by the addition of 10 ml of NaOH (0.1 M). The mixture was stirred continuously at 50 °C for 30 min. the colour of the solution changed to green which confirmed the formation of CuO nanoparticles (see figure 1). Then the solution was centrifuged for 15 min at 3000 rpm and dispersed in distilled water to remove any unwanted biological materials. The prepared CuO nanoparticles were collected and UV-VIS of the solution was measured. The nanoparticles were diluted to avoid errors due to high optical density [20]. The prepared CuO nanoparticles powder thus obtained was oven dried at 80 ˚C overnight [21]. The resultant dried powder was used for the XRD and FT-IR characterization of nanoparticles.

2.3 Characterizations

CuO nanoparticles were synthesized by the green synthesis method using copper sulfate pentahydrate (precursor salt) and Malva Parviflora leaf extract (reducing and stabilizing agents). The crystal structure of the sample was analyzed by using the XRD-6100 diffractometer (Shimadzu), and the patterns were recorded with Copper Kα radiation (λ=1.54060 Å). Molecular analysis of the sample was performed by Fourier transform infrared (FT-IR) spectroscopy using IRAffinity-1S(Shimadzu) spectrometer, recorded in the wavenumber range of 500–4,000 cm^{-1}. The optical characteristics of CuO nanoparticles were characterized by UV-Visible Spectroscopy (JASCO V 670), in the range of 200-800 nm. The optical band gap was determined using Touch's plot method hν versus $(\alpha h\nu)^{1/2}$, where α and hν denote the optical absorption coefficient and photon energy, respectively.

3. Results and discussion

The Formation of CuONPs by using Malva parviflora leaves extract in an aqueous medium, which was ascertained from a change in colour from blue to green. Flavonoid (Rutin) present in the Malva parviflora leaves extract is responsible for the reduction of Cu^{+2} to CuONPs [22], where that the phytochemicals in the plant extracts first form complexes with the copper salt and then reduce the ions to form nanoparticles reported by Mehr et al.[23]. In addition, the change of pH of mixture, it can be realized that basic medium are satisfactory for the synthesis of nanoparticles while acidic mixture is not satisfactory, which that refer to quantity of the bioactive compounds reported by Din et al. [18]. However, other researcher have reported that the synthesis of CuO nanoparticles can be monitored by changes in the colour may be understood in terms of the reaction between copper (II) sulfate pentahydrate and sodium hydroxide to form copper (II) hydroxide (blue), which in turn reacts with the rutin resulting in the formation of dehydrorutin and copper(I) oxide (brown).

$$CuSO_4.5H_2O + 2NaOH \longrightarrow Na_2SO_4 + Cu(OH)_2 + 5H_2O$$

$$2Cu(OH)_2 + \underset{\text{Rutin}}{C_7H_6O_5} \longrightarrow Cu_2O + C_7H_4O_5 + 3H_2O$$

However, as reaction proceeds with time, the copper (I) oxide was formed and finally CuO nanoparticles (greenish-black) formation occur by a series of following reactions [24].

$$Cu_2O + OH^- + H_2O \longrightarrow [Cu(OH)_2]^- + CuOH$$

$$2CuOH \longrightarrow Cu_2O + H_2O$$

$$4CuOH + O_2 \longrightarrow 4CuO + 2H_2O$$

3.1 UV–VIS Spectra analysis

The UV-vis absorption spectra shows the effect of $CuSO_4{\cdot}5H_2O$ concentration on the formation of CuO nanoparticles using aqueous Malva parviflora leaves extract. The UV–Vis absorption spectra of CuO nanoparticles was done at a wavelength range of 200-800 nm as shown in figure1. A concentration variation study of $CuSO_4{\cdot}5H_2O$ using aqueous Malva parviflora leaves extract was carried out with different concentrations of $CuSO_4{\cdot}5H_2O$ (0.001, 0.01, and 0.1M). The surface plasmon resonance (SPR) band for CuO nanoparticles was located around 240-300 nm and it has been reported to undergo red shift with decrease in size [25]. A general trend is that the surface plasmon resonance peak shift towards the higher wavelength region as well as becomes narrower when the concentration value increases. Lakkappa et al. [20] concluded that the rising concentration of the solution results in the formation of nanoparticles with a smaller size. On the other hand, the broadening of the surface plasmon resonance peak indicates the existence of the wider range of size in the solution. Effect of precursor salt solution on nanoparticles synthesis revealed that 0.1M concentration of $CuSO_4{\cdot}5H_2O$ resulted in maximum nanoparticles synthesis with the high intense the SPR absorption peak around 262 nm as compared to the 0.01 M and 0.001 M $CuSO_4{\cdot}5H_2O$, show that in Figure 1. By increasing the concentration of $CuSO_4{\cdot}5H_2O$ from 0.001 to 0.1 M, the reduction rate of copper ions increases dramatically and a large number of particles are formed. Furthermore, at lower of $CuSO_4{\cdot}5H_2O$ concentrations (0.01 and 0.001 M) SPR band was observed broad and weak due to the presence of CuO nanoparticles with broader size distributions. As the amount of $CuSO_4{\cdot}5H_2O$ increased (0.1 M), SPR band became sharper and narrower along with an enhancement in its intensity. This indicates an involvement of narrow size distribution of the CuO nanoparticles, because of the agglomerations of nanoparticles by Van der Waals interactions between neighbouring nanoparticles. These findings are in close agreement with previous reports [26,18]

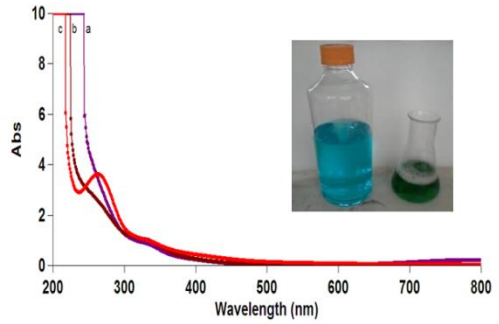


Fig. 1: UV–VIS absorption spectra of CuONPs with different concentrations: (a) 0.001 M; (b) 0.01 M; (c) 0.1 M of aqueous $CuSO_4$ solutions.

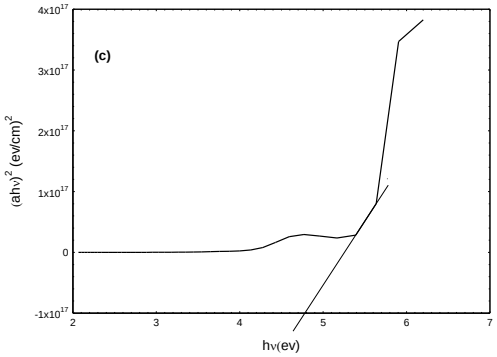


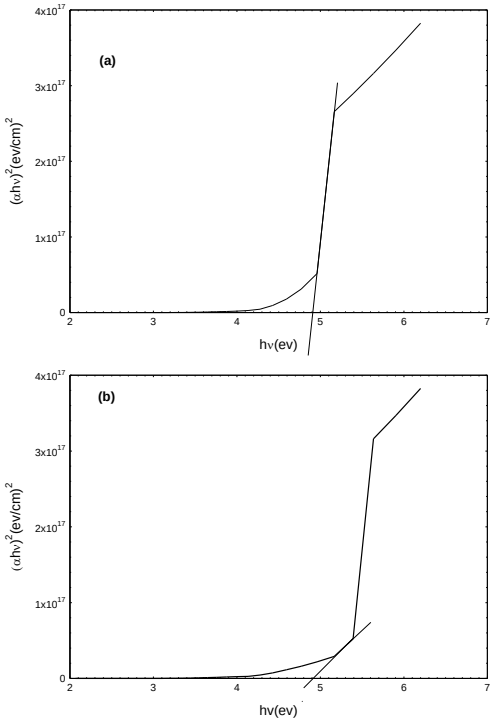
Fig. 2: Direct optical band gap of CuONPs with different concentrations: (a) 0.001 M; (b) 0.01 M; (c) 0.1 M of aqueous $CuSO_4$ solutions.

3.2 Optical band gap analysis

Optical properties of nanoparticles give information about physical properties; such as band gap energy, band structure, and optically active defects. The band gap (E_g) value of the CuO nanoparticles has been studied. The optical band gap of CuO nanoparticles was measured by absorbance coefficient data as a function of wavelength using Tauc relation given as [27]:

$\alpha h\nu = A(h\nu - E_g)^{0.5}$

where α is the absorption coefficient, E_g is band gap energy, A is constant and hν is the photon energy. The plot of $(\alpha h\nu)^2$ versus hν is a linear function of direct allowed transitions in CuO nanoparticles and is shown in figure 2. The energy band gap of the CuO nanoparticles was estimated by fitting a straight line to the linear portion of the curve and Eg is the intercept of the line with the hν-axis. The obtained direct band gap values (a blue shift) are 4.90, 4.87 and 4.77 eV for CuO nanoparticles of concentration 0.001M, 0.01M and 0.1M respectively. Those values are larger than (4.60 eV) for bulk CuO reported by Kannaki et al. [28]. The increased band gap can be attributed to the quantum confinement effect. An associated increase in bandgap with decrease in particle size was also noticed which is a strong indication of the quantum confinement effect [29]. Generally, the change in the band gap value from the bulk structure relies on numerous factors such as the morphology of the particle (size induced quantum confinement), charge carrier concentration, grain size, lattice strain, orbital hybridization by doping the impurity atoms [30].



3.2 X-ray diffraction analysis

The XRD patterns of the CuO nanoparticles synthesized using *Malva parviflora extract were* shown in figure 3. The diffraction pattern for the CuONPs is broad and has no Bragg peaks, indicating an amorphous structure [21]. The broad shoulder peak from 17° to 26° of 2θ values was proposed to be due to which the polyphenols are responsible for reducing and stabilizing nanoparticles. Likewise, the amorphous nature of the synthesized particle was reported [31]. To avoid the interference of polyphenols, the CuONPs was annealed at 400 ^{0}C for 4h. Srivastava et al. [8] reported that the intensity of crystalline peaks increases with temperature, indicating an improvement in the crystallinity.

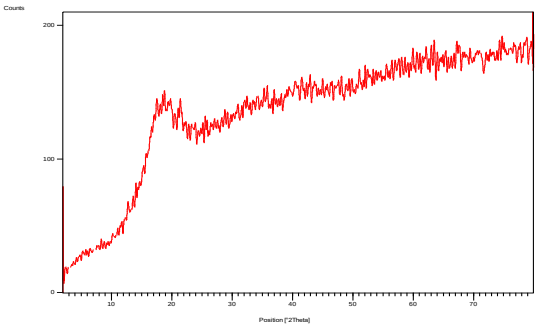


Fig. 3: XRD patterns of CuONPs

3.3 FT-IR spectra analysis

FT-IR spectra analysis was carried out to detect the probable biomolecules that are responsible for the formation of CuO nanoparticles. The comparison of FT-IR spectra between Malva parviflora leaves extract and its complexation with Cu^{+2} ion are shown in figure 4(a,b). The infrared spectra of Malva parviflora extract show a broad absorption band at around 3600 cm^{-1}, corresponding to the hydroxyl groups (O-H) stretching vibrations, which are caused by the phenolic compounds. The C-H stretching vibration of the aromatic group is observed at 3043 cm^{-1}, whereas the absorption bands at 2919 and 2851 cm^{-1} are attributed to asymmetric and symmetric C-H stretching modes of aliphatic hydrocarbon chains. Moreover, the peak at 1734 cm^{-1} corresponds to the C=O stretching vibration, which might arise from the functional groups of ketones, aldehydes, and carboxylic acids. The peak at 1599 cm^{-1} corresponds to C=C stretch in aromatic rings. The peaks at 1466 and 1274 cm^{-1} correspond to the C-O-H in-plane bend and O-H stretching vibrations of polyphenol. Subsequently, the absorption peaks at 1066 and 1012 cm^{-1} are assigned for C-O-C and O-H of the phenolic group. These functional groups prove the presence of polyphenols in Malva parviflora, which might act as reducing and stabilizing agents in the CuO nanoparticles synthesis. The FT-IR spectra reveal that observed bands for functionalized CuO nanoparticles (Figure 4b) are similar to those obtained for Malva parviflora (Figure 4a) with a slight shift, but the intensity of the peaks in range 1200 to 1400 cm^{-1} becomes much decreased. Also, the disappearance of C=O band indicates the reduction of Cu^{+2} taken place. Furthermore, the band involving O-H

vibration at around 3600 cm^{-1} of the phenolic compounds is absent, hence showing deprotonation of the OH group and coordination to the metal. The peak at 527 cm^{-1} should be a stretching of Cu−O [32]. The peak at 527 cm^{-1} indicated the formation of the CuO nanoparticles.

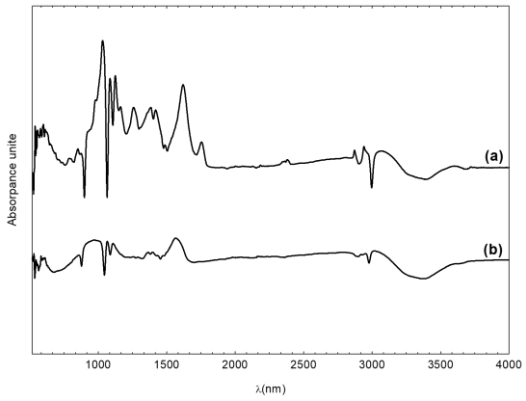
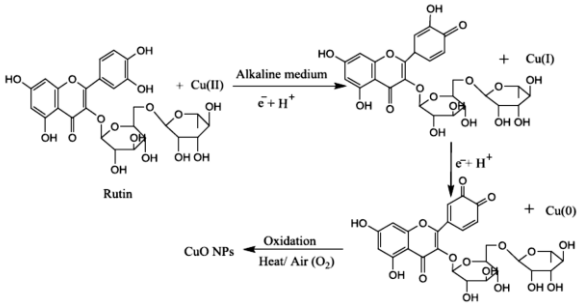


Fig. 4: FT-IR spectra of (a) Malva parviflora extract and (b) CuONPs

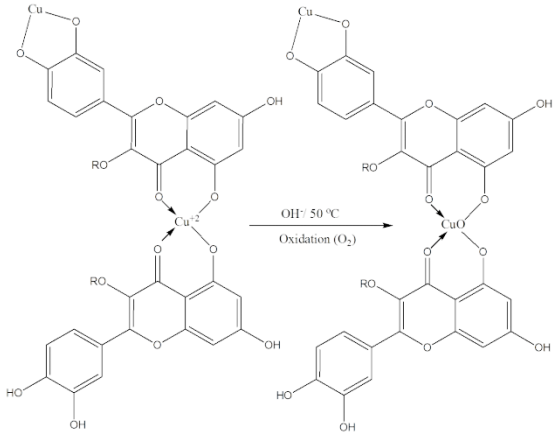
3.4 Mechanism of CuONPs formation

Although various metallic nanoparticles have been synthesized by plant extract, however, the exact mechanism of the synthesis process remains challenges, thus providing opportunities for further study. A proposed mechanism of the CuONPs synthesis from Malva parviflora is shown in scheme 1. The functional groups such as carbonyl and hydroxyl groups present in rutin, which might act as reducing and stabilizing agents in the CuONPs synthesis. Initially, the 3`,4`-dihydroxyl groups present in rutin are responsible for the reduction of copper ions [33]. It has been proposed that hydrogen ions are released during the tautomeric transformation of the enol form of rutin to keto form, which was formed by oxidation after the hydroxyl groups in the B-ring were deprotonated at high pH values [34]. During the synthesis process of CuONPs, Cu^{+2} ions are converted into Cu^0 nuclei. Then the Cu^0 nuclei were concurrently oxidized to the CuO nanoparticles.



Scheme 1: mechanism of formation CuONPs [22]

The capping of CuO nanoparticles by oxidized rutin may have strong chelating activity due to the presence of 5-hydroxyl and 4-carbonyl groups of the C-ring. These groups chelate with Cu(II) ions which protect CuO nanoparticles from agglomeration by following the previous mechanism and also facilitated the formation of coordination bond between the 2nd rutin molecule and rutin-Cu complex [33] as shown in scheme 2. The CuONPs may have been contributed by the adsorption of the electron rich carbonyl groups over the CuONPs surface.



Scheme 2: Stabilization of CuONPs by Rutin

4. Conclusion

In summary, CuO nanoparticles were synthesized with a simple, low cost and the green method by using aqueous Malva parviflora leaves extract as a reducing and stabilizing agents. The UV–VIS and FT-IR studies revealed that the presence of rutin compound may be the significant cause of reducing and stabilizing of CuONPs. Moreover, the optical band gap values of the CuONPs were measured by using Tauc relation. The CuONPs have a relatively large band gap with small size due to the Quantum confinement effect. The XRD studies also displayed that a synthesized nanoparticle exhibits an amorphous structure. Therefore, this CuONPs could be used in the textile industry and water treatment.

Abbreviations

CuONPs: cupric oxide nanoparticles
FT-IR: Fourier transform infrared spectroscopy
SPR: surface plasmon resonance
UV-VIS: Ultraviolet Visible spectroscopy
XRD: X-ray diffraction analysis

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5. References

[1]- Huang, H., Yu, Q., Ye, Y., Wang, P., Zhang, L., Gao, M., Peng, X. and Ye. Z., (2012), Thin copper oxide nanowires/carbon nanotubes interpenetrating networks for lithium ion batteries., Cryst Eng Comm., **14** (21), 7294–7300. DOI: 10.1039/C2CE25873K

[2]- Ramgir, N., Datta, N., Kaur, M., Kailasaganapathi, S., Debnath, A.K., Aswal, D. and Gupta, S., (2013), Metal oxide nanowires for chemiresistive gas sensors: issues, challenges and prospects., Colloid Surface A., **439**: 101–116. DIO:10.1016/j.colsurfa.2013.02.029

[3]- Hong, L., Liu, A.L., Li, G.W., Chen, W. and Lin, X.H., (2013), Chemiluminescent cholesterol sensor based on Peroxidase like activity of cupric oxide nanoparticles., Biosens Bioelectron., **43**, 1-5. DIO: 10.1016/j.talanta.2012.06.061

[4]- Dagher, S., Haik,Y., Ayesh, A. I. and Tit, N., (2014), Synthesis and optical properties of colloidal CuO nanoparticles., J Luminesce., **151**, 149-154. DOI: 10.1016/j.jlumin.2014.02.015

[5]- Hosseinpour, M., Ahmadi, S.J., Mousavand, T. and Outokesh, M.J., (2010), Production of granulated-copper oxide nanoparticles for catalytic application., J Mat Res., **25** (10), 2025-2034. DOI: 10.1557/JMR.2010.0262.

[6]- Norzaee, S., Djahed,B., Khaksefidi,R. and Mostafapour,F.K., (2017), Photocatalytic degradation of aniline in water using CuO nanoparticles., Journal of Water Supply: Research and Technology-Aqua., **66** (3), 178–185. DOI:10.2166/aqua.2017.104

[7]- Sankar, R., Maheswari, R., Karthik, S., Shivashangari, K.S. and Ravikumar, V., (2014), Anticancer activity of Ficusreligiosa engineered copper oxide nanoparticles., Mater. Sci. Eng. C., **44**, 234-239 DOI: 10.1016/j.msec.2014.08.030

[8]- Srivastava, S., Kumar, M., Agrawa, A. and Dwivedi, S. K., (2013), Synthesis and Characterization of Copper Oxide Nanoparticles., IOSR Journal of Applied Physics (IOSR-JAP)., **5**(4), 61-65.

[9]- Ahamed, M., Alhadlaq, H.A., Khan, M., Karuppiah, P. and Al-Dhabi, N.A. (2014), Synthesis, Characterization, and Antimicrobial Activity of Copper Oxide Nanoparticles., Journal of Nanomaterials., **3**, 33-42. DOI:10.1155/2014/637858

[10]- Swarnkar, R.K., Pandey, J.K., Soumya, K.K., Dwivedi, P., Sundaram, S., Prasad, S. and Gopal, R., (2016), Enhanced antibacterial activity of copper/copper oxide nanowires prepared by pulsed laser ablation in water medium., Applied Physics A., **122**, 704 DOI:10.1007/s00339-016-0232-3

[11]- Akintelu, S. A., Folorunso, A. S., Folorunso, F. A. and Oyebamiji, A. K., (2020), Green synthesis of copper oxide nanoparticles for biomedical application and environmental remediation., Heliyon, **6**(7). DOI.org/10.1016/j.heliyon.2020.e04508

[12]- Gebremedhn, K., Kahsay, M.H. and Aklilu, M., (2019), Green Synthesis of CuO Nanoparticles Using Leaf Extract of Catha edulis and Its Antibacterial Activity., Journal of Pharmacy and Pharmacology, **7**, 327-342. DOI:10.17265/2328-2150/2019.06.007

[13]- Iravani, S., (2011), Green synthesis of metal nanoparticles using plants., Green Chem., **13**, 2638-2650.DOI: 10.1039/C1GC15386B

[14]- Farhan, H., Rammal, H., Hijazi, A. and Badran, B., (2012), Preliminary phytochemical screening and extraction of polyphenol from stems and leaves of a Lebanese plant *Malva parviflora* L., Int J Curr Pharma Res., **4**, 55-59.

[15]- Singh, A. and Ethnomedicinal, N., (2017), Antimicrobial and Pharmacological aspects of Malva parviflora Linn.: A review., The Journal of Phytopharmacology., **6**(4), 247-250.

[16]- Shehata, H.S., and Galal, T.M., (2014), Phytosociology and phytochemical screening of the medicinal weed Malva parviflora L., Life Science Journal., **11**(6), 458-468.

[17]- Al-Qarawi, K.K. and Al-Obaidi, H.M.R., (2018), Detection of the active compounds in the leaves of the Common mallow plant Malva parviflora L. using GC-MS and HPLC technology., Kufa Journal For Agricultural Sciences., **10** (4), 87-95.

[18]- Din, M. I., Arshad, F., Rani, A., Aihetasham, A., Mukhtar, M., Mehmood, H. A., (2017), Single Step Green Synthesis Of Stable Copper Oxide Nanoparticles As Efficient Photo Catalyst Material., Journal of Optoelectronics and Biomedical Materials., 9(1)1: 41 – 48.

[19]- Daniel SCGK, Nehru K, Sivakumar M (2012) Rapid biosynthesis of silver nanoparticles using Eichornia crassipes and its antibacterial activity. Curr Nanosci 8(1):125–129. DOI: 10.2174/1573431711208010125

[20]- Lakkappa, B.A., Jasmith, S.C., Prabhuodeyara, M.G., (2017), Effect of Concentration and pH on the Size of Silver Nanoparticles Synthesized by Green Chemistry., Organic & Medicinal Chem IJ., **3**(5):1-5. DOI: 10.19080/OMCIJ.2017.03.555622

[21]- Rani Verma, P., and Khan, F., (2019), Green approach for biofabrication of CuO nanoparticles from Prunus amygdalus pericarp extract and characterization., Inorganic and Nano-Metal Chemistry., 49(3), 69-74. DOI:10.1080/24701556.2019.1601738

[22]- Nasrollahzadeh M, Sajadi SM., (2015), Green synthesis of copper nanoparticles using Ginkgo biloba L. leaf extract and their catalytic activity for the Huisgen [3 + 2] cycloaddition of azides and alkynes at room temperature., J Colloid Interface Sci., 457:141–7.DOI:10.1016/j.jcis.2015.07.004.

[23]- Mehr E.S., Sorbiun M., Ramazani A., Fardood S.T., (2018), Plant-mediated synthesis of zinc oxide and copper oxide nanoparticles by using Ferulago angulata (Schlecht) Boiss extract and comparison of their photocatalytic degradation of Rhodamine B (RhB) under visible light irradiation., J. Mater. Sci. Mater. Electron, 29, 1333–1340. DOI: 10.1007/s10854-017-8039-3

[24]- Qamar, H., rehman, s.,Chauhan, D. K.,Tiwari, A.K., upmanyu, V., (2020), Green Synthesis, Characterization and Antimicrobial Activity of Copper Oxide, Nanomaterial Derived from Momordica charantia., International journal of nanomedicine., 15, 2541-2553. DOI: 10.2147/IJN.S240232.

[25]- Abboud, Y., Saffaj, T., Chagraoui, A., El Bouari, A., Brouzi, K., Tanane, O., and Ihssane, B., (2014), Biosynthesis, characterization and antimicrobial activity of copper oxide nanoparticles (CONPs) produced using brown alga extract (Bifurcaria bifurcata)., Applied Nanoscience., 4(5), 571-576.

[26]- Ider, M., Abderrafi, K., Eddahbi, A.,Ouaskit, S., and Kassiba, A., (2017), Silver metallic nanoparticles with surface plasmon resonance: Synthesis and characterizations., Journal of Cluster Science, **28**(3), 1051-1069. DOI 10.1007/s10876-016-1080-1

[27]- Mott N.F. and E.A. Davies, Electronic Processes in Non-Crystalline Materials, second Edition. Clare don Press, Oxford, 1979.

[28]- Kannaki, K., Ramesh, P.S., Geetha, D., (2012), Hydrothermal synthesis of CuO Nanostructure and Their Characterizations., Int J Sci Eng Res., **3**(9), 1-4.

[29]- Manzoor, U., Islam, M., Tabassam, L., & Rahman, S. U., (2009), Quantum confinement effect in ZnO nanoparticles synthesized by co-precipitate method. Physica E: Low-Dimensional Systems and Nanostructures., 41(9), 1669-1672.DOI:10.1016/j.physe.2009.05.016

[30]- Annathurai, S., Chidambaram, S., Baskaran, B., Venkatesan, G. K. D. P., (2019), Green Synthesis and Electrical Properties of p-CuO/n-ZnO Heterojunction Diodes., Journal of Inorganic and Organometallic Polymers and Materials., **29** (2), 535-540. DOI:10.1007/s10904-018-1026-1

[31]- Wang, Z. and An, P. (2017), Characterization of Copper Complex Nanoparticles synthesized by Plant Polyphenols. bioRxiv., 1-18. DOI:10.1101/134940

[32]- Karthik, K., VictorJaya, N., Kanagaraj M., Arumugam S., (2011), Temperature-dependent magnetic anomalies of CuO nanoparticles., *Solid State Commun*., **151**(7), 564-568. DOI: 10.1016/j.ssc.2011.01.008

[33]- Bai, Y., Song, F., Chen, M., XING, J., LIU, Z., and LIU, S., (2004), Characterization of the rutin-metal complex by electrospray ionization tandem mass spectrometry. Analytical sciences. **20**(8), 1147-1151. DOI: 10.2116/analsci.20.1147

[34]- Souza, R.F.V. and Giovani, W.F., (2004), Antioxidant properties of complexes of flavonoids with metal ions., Redox Report., **9**(2), 97-104. DOI:10.1179/135100004225003897