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Onion Seed Essential Oil-Grafted Zerovalent Copper Nanoparticles as Promising Material for Supercapacitor Electrodes in Energy Storage Device

RAMANJANEYULU KONGARA[1,*], N. USHA RANI[2] and T.S.R.K. PRASAD RAO[3]

[1]Department of Electronics and Communication, P.V.P. Siddhartha Institute of Technology, Vijayawada-520007, India
[2]Department of Freshman Engineering, P.V.P. Siddhartha Institute of Technology, Vijayawada-520007, India
[3]Department of Chemistry, P.B. Siddhartha College of Arts & Science, Vijayawada-520010, India

*Corresponding author: E-mail: kongara.raman@gmail.com

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Nanobiotechnology was considered as unique branch of contemporary science that facilitates paradigm shift in the field of material research. This study utilizes easy, convenient and cost-effective essential oil isolated from the onion seed as reducing agent for fabrication of copper nanoparticles and applicability of synthesized nanoparticles as supercapacitor electrodes. In the synthesis process, solution colour turned from pale blue to green and then it reach reddish brown colour due to reduction in Cu^{2+} in copper sulphate in to Cu^{0} nanoparticles that exhibit characteristic wavelength maxima of 292 nm on UV-visible spectrophotometer. The GCMS analysis confirms the involvement of 2-phenylethanol, 1-hexanol, α-phellandrene, 2-pentylfuran, palmitic acid and trimethylbenzene from essential oil in the formation of nanoparticles. The particles were in spherical shape with most abundant particle size of ~ 17 nm having monoclinic phase crystal structure with 80.95% copper content. The supercapacitor application of the synthesized nanoparticles was investigated through electrochemical investigation. The specific conductance of synthesized nanoparticles was assessed through cyclic voltammetry that exhibit an impressive response of 364, 332, 311, 255 and 206 F/g, respectively at 10, 20, 40, 60 and 100 mV/s. The specific capacitance of nanoparticles was confirmed as 364 F/g with 97.1% retention capacity after 6000 cycles. The findings indicate that copper oxide nanoparticles, obtained biologically, exhibit promising applicability with well-suitability for use in the energy storage devices. Overall, the results of the current study show that the biologically produced copper oxide nanoparticles have intriguing uses as supercapacitor electrodes.

Keywords: Copper nanoparticles, Onion seeds, Essential oil, GC-MS analysis, Supercapacitor electrodes.

INTRODUCTION

Supercapacitors, also known as ultracapacitors or electrochemical capacitors, are energy storage devices that bridge the gap between traditional capacitors and batteries. They store and release energy electrostatically, offering a unique set of characteristics that make them valuable in various applications [1]. Supercapacitors offer several advantages such as high power density, rapid charge-discharge and longer cycle life compared to batteries, efficient energy storage, low internal resistance and wide operating temperature that make them valuable in specific applications. Based on the energy storage mechanism, supercapacitors were divided as electrical double-layer capacitors (EDLCs) and pseudo-capacitors. Among various supercapacitors including conventional and EDLCs, pseudo-capacitors exhibit significantly high energy density and specific capacitance [2]. Hence, researchers were concentrating to enhance performance of supercapacitors by creating pseudo-capacitors. The oxides of transition metals serve as active pseudo-capacitors due to its high abundance, low price, enhanced conductivity, multi-oxidation states and stability. Among various metal oxide, copper oxides have consistently stood out as particularly appealing among metallic oxides due to its brilliant electrochemical performance, low price, eco-friendly nature and enticingly high capacitance [3].

Green synthesis refers to the eco-friendly and sustainable methods used to produce nanoparticles, avoiding the use of harmful chemicals and minimizing environmental impact. Green synthesis methods often involve the use of plant extracts, microorganisms or other natural resources to reduce and stabilize metal ions, leading to the formation of nanoparticles. This approach is gaining attention due to its potential for reducing the ecological footprint of nanomaterial synthesis [4,5].

The use of green synthesized nanoparticles as pseudo-capacitors is an interesting and emerging area of research in nanotechnology and energy storage. The combination of green synthesis and pseudo-capacitors holds promise for advancing energy storage technologies with a focus on sustainability [6,7]. Ongoing research is likely to uncover new green synthesis methods, novel materials and optimized device designs for improved performance and widespread practical applications [8]. Onion seeds, derived from the onion plant (*Allium cepa*), are small, dry seeds that serve as the reproductive units of the onion flower [9]. They are tiny, black or dark brown and roughly triangular or oval in shape [10]. Onion seeds have a distinct flavour that is different from the onion bulb itself. They can have a slightly nutty, earthy or peppery taste, depending on the specific variety [11,12]. Onion seed oil contains various chemical constituents that contribute to its unique properties and poten-tial health benefits. Onion seed oil is rich in sulfur-containing compounds, including various organosulfur compounds [13,14].

In the process of synthesis of nanoparticles, the plant derived essentials oils which are concentrated hydrophobic liquids containing volatile aroma compounds act as both reducing and stabilizing agents. In literature, various plant essential oils for the fabrication of metal nanoparticles including silver [15-21], titanium dioxide [22], iron [23], gold [24], magnesium [25], copper [26], *etc*. are reported. Moreover, several researchers also explored the utility of green synthesized nanoparticles in the energy storage applications [27-31] but the applicability was not adequately explored. In view of this, this study was proposed to utilize onion seed essential oil mediated copper nanoparticles as supercapacitor electrodes in energy storage device.

EXPERIMENTAL

The onion seeds were purchased from the local grocery store, Vijayawada, India. The analytical reagent grade chemicals including copper sulfate ($CuSO_4$), polyethylene glycol (PEG) 8000, sodium borohydride ($NaBH_4$) and ascorbic acid were brought from Merck Chemicals, India.

Extraction of essential oil from onion seeds: The demineralized water was utilized as extracting medium for extracting essential oil from onion seeds. Initially, the seeds were surface cleaned twice with demineralized water to remove impurities and dust particles. Then the seeds were bolted with tissue paper to remove water particles and grinded with mechanical grinder to obtain seed powder. An approximate 150 g of seed powder was hydrodistilled with 1.5 L demineralized water at 80 ºC for 4 h in a Clevenger apparatus (Borosil®). The extracted essential oil was separated carefully and was characterized by pale yellow colour with deeply pungent smell. The separated oil was stored at 6 ºC in a refrigerator and utilized for fabrication of nanoparticles.

GC-MS analysis: The chemical analysis of essential oil and it mediated copper nanoparticles was performed on Agilent (USA) 7890 model instrument equipped with DB-624 capillary (30 m × 0.25 mm; 0.25 µm) column and helium gas as carrier gas at 1.2 mL/min flow with 1:4 split ratio. Initially, the oven temperature was maintained at 60 °C for 3 min and then raised to 220 ºC at 5 ºC/min raise rate and the same was maintained for 1 min. The sample at 0.2 µL quantity was precisely injected through injector at 250 ºC. The electrospray ionization at 70 eV was utilized for mass spectrometer detection of compounds and spectrum was recorded at 40 to 350 amu. The chemical constituents were identified by correlating the retention indices of each constituent related to *n*-alkanes and mass fragmentation pattern of individual compound correlated with National Institute of Standards and Technology (NIST) library.

Synthesis of copper nanoparticles: An accurately weighed 20 mL of PEG solution was added to 500 mL beaker containing 100 mL of $CuSO_4$ (0.1 M) solution. The content in the beaker was stirred in a magnetic stirrer at room temperature for 1 h. Then, 40 mL of 0.5 M aqueous ascorbic acid solution was added and continued the stirring for 30 min at 5000 rpm at 100 ºC followed by adding 80 mL of $NaBH_4$ solution. Then 10 mL of extracted onion seed essential oil was added slowly to the reaction mixture with constant stirring for 30 min at 5000 rpm. The resultant particles were collected by filtration followed by washing with distilled water and drying [26]. The obtained particles were characterized and assessed for its applicability as supercapacitor electrodes in energy storage devices.

Characterization: The optical properties of onion seed essential oil and oil mediated copper nanoparticles were evaluated by employing double beam UV-visible spectrophotometer (JASCO, V-560, Japan) in the 200-800 nm scan range. The essential oil chemical constituents involved in the formation of copper nanoparticles were assessed through GC-MS analysis. The structural characterization of copper nanoparticles was performed with TEM (transmission electron microscopy) and SEM (scanning electron microscope) coupled with EDX (energy-dispersive X-ray spectroscopy) techniques. The nanoparticles were washed in methanol followed by distilled water and then fixed to carbon-coated copper grids and these grids were subjected to TEM (Jeol JEM 2100, Japan) analysis and instrument was operated at 120 keV. SEM (Jeol 6390LA, Japan) coupled with EDX (OXFORD XMX-N, UK) was performed to evaluate the particle size along with elemental composition of copper nanoparticles. The instrument was operated at 0.5 to 30 kV as accelerating voltage and Tungsten lamp as energy source. The Bruker (USA) D8 advance X-ray diffraction (XRD) instrument that utilizes Cu$K\alpha$ radiation was employed for evaluating the crystal size of nanoparticles and analysis was conducted at 2θ of 20-100º. The zeta potential and particle size of synthesized nanoparticles was evaluated on Brookhaven (DR-525, USA) 90Plus nanoparticle size analyzer.

Electrochemical characterization: The electrochemical characterization of onion seed essential oil mediated copper nanoparticles was evaluated by employing electrochemical workstation (CHI660E, USA). This study utilizes working electrode (Ni foam), auxiliary electrode (platinum wire) and reference electrode (Ag/AgCl). In this, an accurately weighed 1 mg of synthesized copper nanoparticles were mixed with

0.5 mL of *N*,*N*-methyl pyrrolidone and then converted in to a slurry paste using 10% polyvinylidene fluoride (PVF). This slurry was pasted on the working electrode (1 cm × 1 cm) and dried at 25 ºC to 2 h. In this experiment, KOH (3 M) solution as electrolyte was used. The cyclic voltammetry experiment was conducted between 0 to 0.65 V at different scan rates. The galvanostatic charge-discharge (GCD) curves were measured in 0 to 0.6 V voltage range at various current densities. The electrochemical impedance spectroscopy (EIS) experiment was conducted with fixed amplitude (5 mV) and frequency (0.001 kHz). The specific capacitance of electrode was determined using eqn. 1:

$$Cs = \frac{i\Delta t}{m\Delta v}$$

where i represents constant current; Δt is the galvanostatic discharge time (s); m represents the sample weight (mg) and Δv is the potential window applied (volts)

The capacitance (c) of the synthesized nanoparticles, expressed as F/g, was calculated using eqn. 2:

$$c = \frac{1}{mv(V_c - V_a)\int_{V_a}^{V_c} I(V)dV}$$

where I represents the applied current in A; $V_c - V_a$ is the potential range; V represents the potential rate (mV/s) and m is the nanoparticles loaded on electrode at 1 cm^2.

RESULTS AND DISCUSSION

This study intended to fabricate copper nanoparticles employing the chemical constituents present in essential oil extracted from seeds of onion as reducing and capping agent. The addition of essential oil, PEG, $NaBH_4$ and ascorbic acid to metal solution initiates the fabrication of nanoparticles. Keeping in consideration of high yield of nanoparticles with less time, the pH of fabrication reaction mixture was varied at various pH values ranging from 4 to 10. Based on yield and time for the formation of nanoparticles, the reaction mixture pH at 8 was proved to be appropriate. During this process, solution colour turned from pale blue to green and then it reach reddish brown colour due to reduction in Cu^{2+} to Cu^0 nanoparticles. This change in colour was monitored with UV-visible absorption spectrophotometer in the 200-800 nm scan range. In the process of formation of copper nanoparticles, the 'core electrons' interband transition was observed that exhibit broad peak at 292 nm and such absorption band was not visualized in scan spectrum of extracted essential oil. Similar adsorption were also observed in various findings reported in the literature [26,31].

The optical band gap of nanoparticles is size-dependent. As the size of copper nanoparticles decreases, the band gap increases, leading to shifts in the absorption spectra (Fig. 1). Understanding and manipulating the optical band gap allow researchers to tailor the optical properties of copper nanoparticles for various applications. It was essential for applications in electronics, as it influences the electrical conductivity and charge carrier dynamics of copper nanoparticles. Hence, following the Tauc classical approach (eqn. 3), the optical band gap (E_g) of synthesized nanoparticles was calculated.

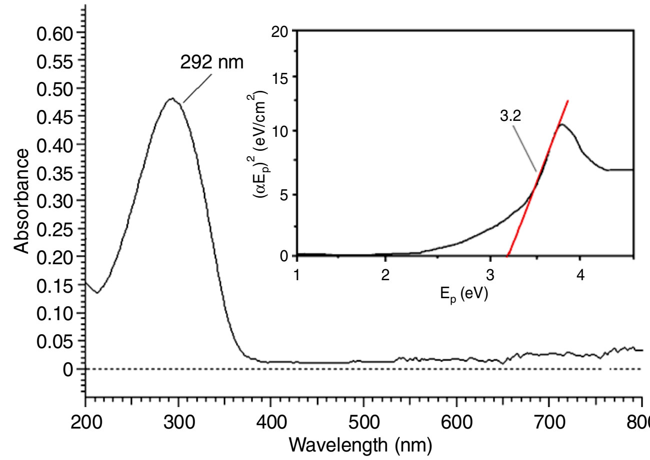


Fig. 1. Absorption spectrum observed by dispersing the synthesized copper nanoparticles in water and measuring absorption spectra with 0.1 cm cuvette in 200- 800 nm range; Inset displayed the graph observed by plotting $(\alpha E_p)^2$ against E_p during band gap calculation

$$\alpha E_p = K(E_p - E_g)^{1/2}$$

where, E_p = discrete photo energy; K = constant.

The results confirmed that the synthesized copper nanoparticles exhibit a band gap of 3.2 eV. A significant high band gap for the synthesized copper nanoparticles enable the tailoring of their properties for a wide range of applications, including electronics, sensing, catalysis and biomedical uses.

The chemical composition of isolated onion seed essential oil and synthesized nanoparticles was evaluated using GC-MS analysis. The GC-MS chromatogram of copper nanoparticles as shown in Fig. 2 confirms presence of components such as 2-phenylethanol, 1-hexanol, α-phellandrene, 2-pentylfuran, palmitic acid and trimethylbenzene. These compounds observed with high % abundance in the extracted essential oil and acted as capping and reducing agents during the formation of copper nanoparticles. Table-1 presents the details of essential oil based phytochemical constituents identified in the formed copper nanoparticles.

Morphological studies: The particle surface activity, size and shape of nanoparticles were investigated with TEM analysis. The experiment was conducted by focusing the nanoparticle material at two different scales such as 1 μm and 100 nm. In 1 μm scale range, clear particle shape and size was observed whereas clear particles were noticed at 100 nm scale. The clear microscopic observation proved that the particles were spherical shape with most abundant particle size of ~ 17 nm (Fig. 3a). These spherical surface particles provide high surface area with more actives sites for electrochemical reactions in supercapacitor which leads to enhanced capacitance of supercapacitor. Further the spherical size facilitates high charge and discharge rates which enhance the overall conductivity of supercapacitor. In SAED (selected area electron diffraction) analysis (Fig. 3b) confirms the existence of intermediate points in concentration circles proves the crystallinity of synthesized nanoparticles.

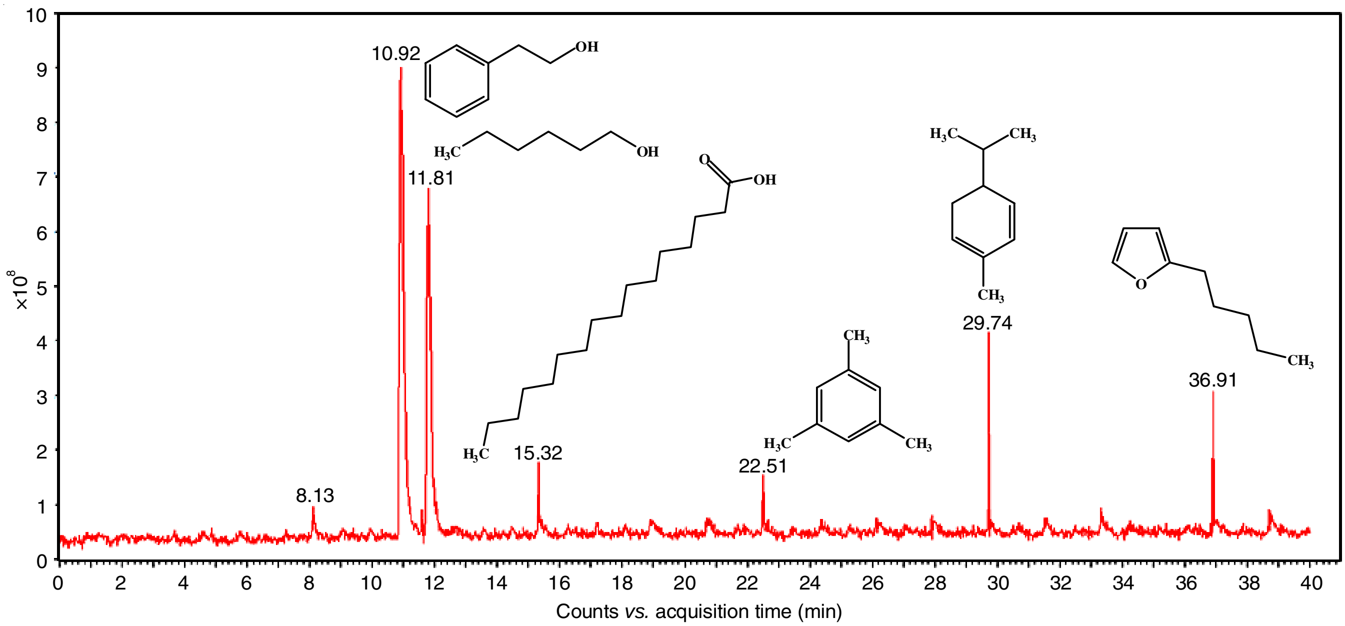
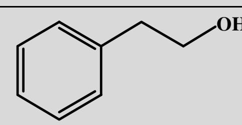
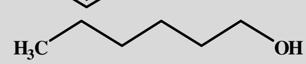
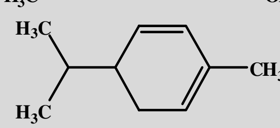
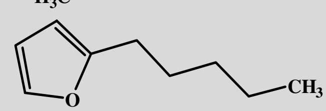
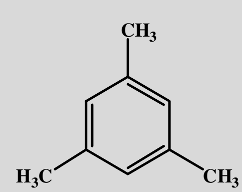


Fig. 2. GCMS chromatogram of copper nanoparticles synthesized using essential oil extracted from onion seed

TABLE-1
CHEMICAL CONSTITUENTS IDENTIFIED IN GCMS ANALYSIS OF COPPER NANOPARTICLES SYNTHESIZED WITH ESSENTIAL OIL EXTRACTED FROM ONION SEEDS

Rt (min)	m.f.	m.w. (g/mol)	Compound name	Structure
10.92	$C_8H_{10}O$	122.16	2-Phenylethanol	
11.81	$C_8H_{14}O$	102.17	1-Hexanol	
29.74	$C_{10}H_{16}$	136.23	α-Phellandrene	
36.91	$C_9H_{14}O$	138.20	2-Pentylfuran	
15.32	$C_{16}H_{32}O_2$	256.42	Palmitic acid	
22.51	C_9H_{12}	120.19	Trimethylbenzene	

The zeta potential of synthesized copper nanoparticles was studied to evaluate the same and opposite charged particles repulsion in dispersion solution in terms of charge and magnitude. When the zeta potential is sufficiently high, the nanoparticles repel each other, reducing the likelihood of aggregation. The zeta potential of synthesized copper nanoparticles was found to be -27.9 mV (Fig. 3c), which confirms the stability nanoparticles at ambient temperature. The results are in good argument with various findings reported in literature [26,31, 32].

The structural information along with the crystallinity of copper nanoparticles synthesized with onion seed essential oil was assessed by performing the XRD experiments. Based on the experimental results, Bragg's law equation and Scherrer's formula were utilized for evaluating interplanar spacing (d) and crystal size (D) of synthesized copper nanoparticles, respectively.

$$n\lambda = 2d \sin\theta$$

$$D = \frac{K\lambda}{\beta\cos\theta} \times 100$$

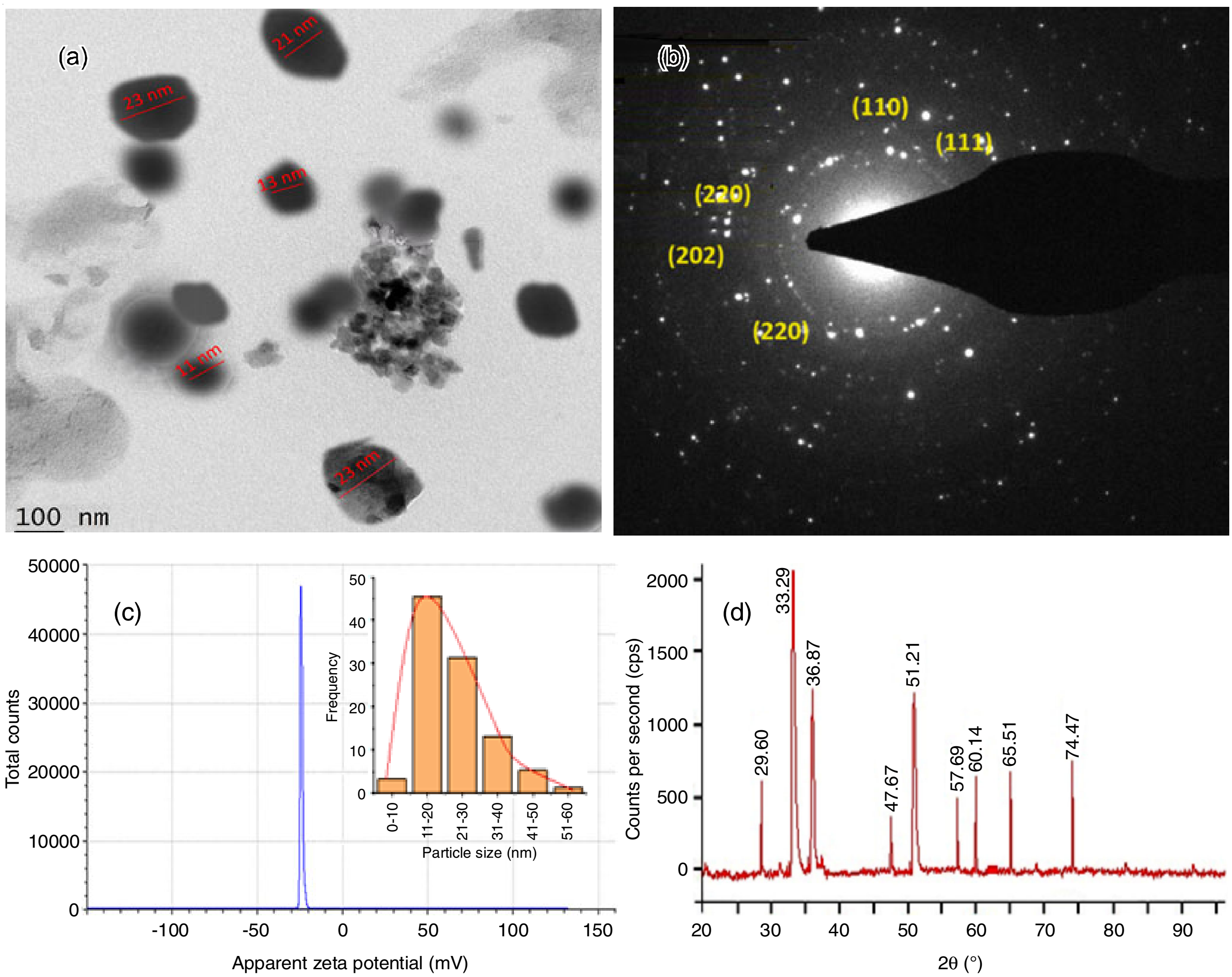


Fig. 3. Characterization of bio-synthesized copper nanoparticles synthesized using onion seed essential oil

where λ presents X-ray wavelength studied; k is the shape constant, θ represents Bragg's angle and β is the full width half maximum.

The diffraction peaks (Fig. 3d) at 29.60° (110), 33.29° (002), 36.87° (111), 47.67° (200), 51.21° (202), 57.69° (002), 60.14° (113), 65.51° (220) and 74.47° (004) correlated with the planes of monoclinic phase crystal structure confirmed that the synthesized copper nanoparticles were in monoclinic phase crystal structure. The crystal structure of copper nanoparticles were in accordance with standard JCPDS card No. 01-080-1268 and the results were also well-correlated with the findings reported by other authors [26,31,32]. The most abundance particle size range was observed to be 13 to 26 nm with ~ 17.6 nm as average particle size. The absence of unassigned diffraction peaks in the XRD spectrum indicates the absence of contaminants in the synthesized nanoparticles, suggesting a high level of purity.

The EDX studies were performed to evaluate the elemental conformation along with weight and atomic percentage of synthesized copper nanoparticles. In EDX spectra (Fig. 4), peak representing to copper was identified at ~ 8.05 keV. The elements correspond to the phytochemical constituents such as carbon (~ 6.04%) and oxygen (~ 13.01%) were identified at ~ 0.28 keV and ~ 0.51 keV, respectively. There is no peaks represents to other elements was observed in the spectrum suggest that the formed nanoparticles possesses significantly high purity.

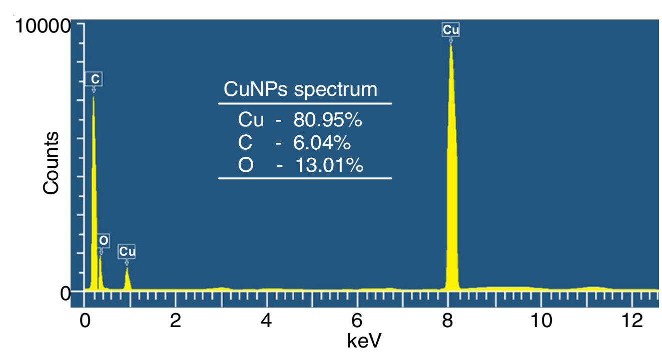


Fig. 4. EDX spectrum of bio-synthesized copper nanoparticles synthesized using onion seed essential oil

Electrochemical studies: The traditional three-electrodes system employing KOH as electrolyte solution was utilized to perform the electro-chemical analyses. The current response of electrochemical system as a function of the applied potential was evaluated using cyclic voltammetry. This study involves the usage of Ni foam electrode modified with 1 mg of synthesized copper nanoparticles at 25 to 100 mV/s scan range and 0–0.65 V potential range (Fig. 5a). Based on results, it was confirmed that as the scan rate increases gradually, the current value also increased accordingly. The permanent Faradic redox current responses of synthesized copper nanoparticles loaded Ni foam exhibit significantly better response than Ni foam. The cyclic voltammetry curve of synthesized nanoparticles exhibited largest integral area with significantly high current density in cathodic as well as anodic peaks (Fig. 5b).

The galvanostatic charge discharge (GDC) curves (Fig. 5c) of synthesized copper nanoparticles was studied at 1 to 5 current densities which was expressed as current applied (A)/electrode material quantity (g). The stabilization of charge/discharge time was observed when the current density reduced. Based on the cyclic voltammetry response, the specific conductance was found to be 364, 332, 311, 255 and 206 F/g, respectively at 10, 20, 40, 60 and 100 mV/s, whereas specific conductance from GDC curves was observed to be 630, 511, 425, 254 and 123 F/g, respectively at current densities of 1 to 5 (Fig. 5d). The copper nanoparticles/nanocomposites reported recently by various researchers was compared with the results achieved in this study (Table-2) and based on this it was confirmed that the nanoparticles synthesized in this study produce best efficient capacitance then various researchers reported in literature.

The electrode cycle stability study was also performed to investigate the long-term performance and stability of the electrodes that was utilized as energy storage devices such as batteries and supercapacitors. The electrodes were investigated under to check the repeated charge and discharge cycles to perform the device's functioning conditions over an extended period. The electrode, after preparation, underwent 6000 charge/discharge cycles at 1 A/g current density and retained 97.1% of its initial capacity (Fig. 6a). The electrochemical impedance spectroscopy (EIS) was performed to investigate the changes in the impedance of an electrode over repeated cycles, providing insights into the stability and performance of the electrode material. This study was performed using KOH (1 M) as electrolyte in between 0.01 Hz to 100 kHz with a potential of 20 mV. Based on EIS results (Fig. 6b), the solution resistance (R_s) of 2.81 Ω and charge transfer resistance (R_{ct}) of 14.57 Ω was achieved. The lower R_s values were noticed in this study indicate the electric conductivity efficiency and current collector attachment of material.

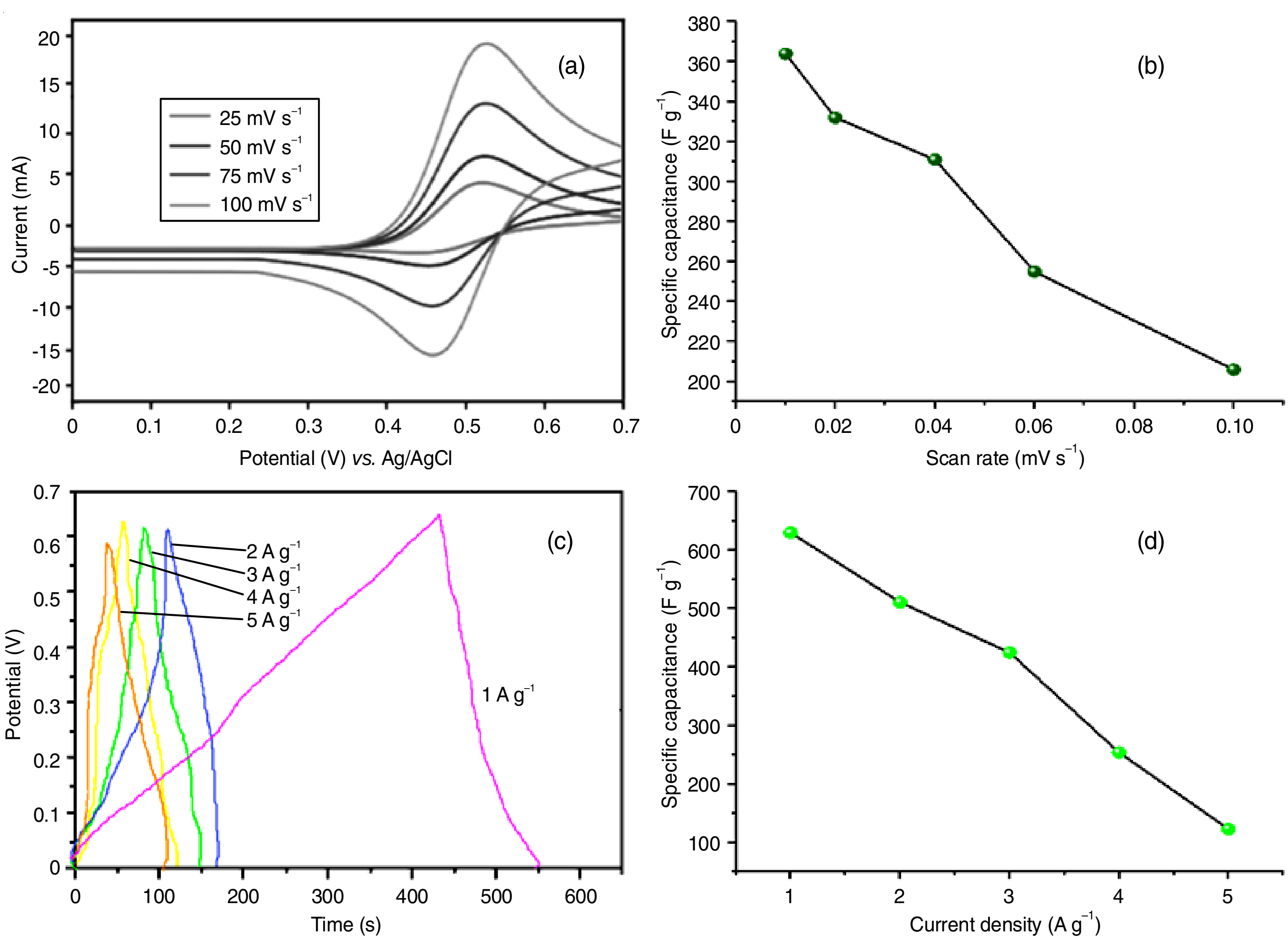


Fig. 5. Results observed during electrochemical tests of synthesized copper nanoparticles in which (a) will be the cyclic voltammetry responses noticed at various scan rates such as 25, 50, 75 and 100 mV/s, (b) represents calculated specific capacitance, (c) presents the GDC curves synthesized copper nanoparticles at various current densities and (d) provides observed specific capacitance results calcuated at various current densities

TABLE-2
CORRELATION OF THESE STUDY FINDINGS WITH THE LITERATURE RELATED TO THE APPLICABILITY OF BIOSYNTHESIZED COPPER NANOPARTICLES AS SUPERCAPACITOR

Electrode material	Specific conductance (F/g)	Retention of capacitance (%)	Electrolyte	Ref.
CuO NPs	364	98.7	KOH	This study
Cu_2O/reduced grapheme oxide	195	79.0	KOH	[33]
CuONPs/activated carbon	245	99.5	Na_2SO_4	[34]
CuO-graphene oxide	82.1	98.0	KOH	[35]
Cu_2O	87	74.0	Na_2SO_4	[36]
$CuFeS_2$	501	82.0	Na_2SO_4	[36]
Carbon nanotubes @TFcP/Cu	280	80.0	H_2SO_4	[37]
CuO	2.14	Not reported	$NaHCO_3$	[38]
CuO-reduced grapheme oxide	137	Not reported	Na_2SO_4	[39]

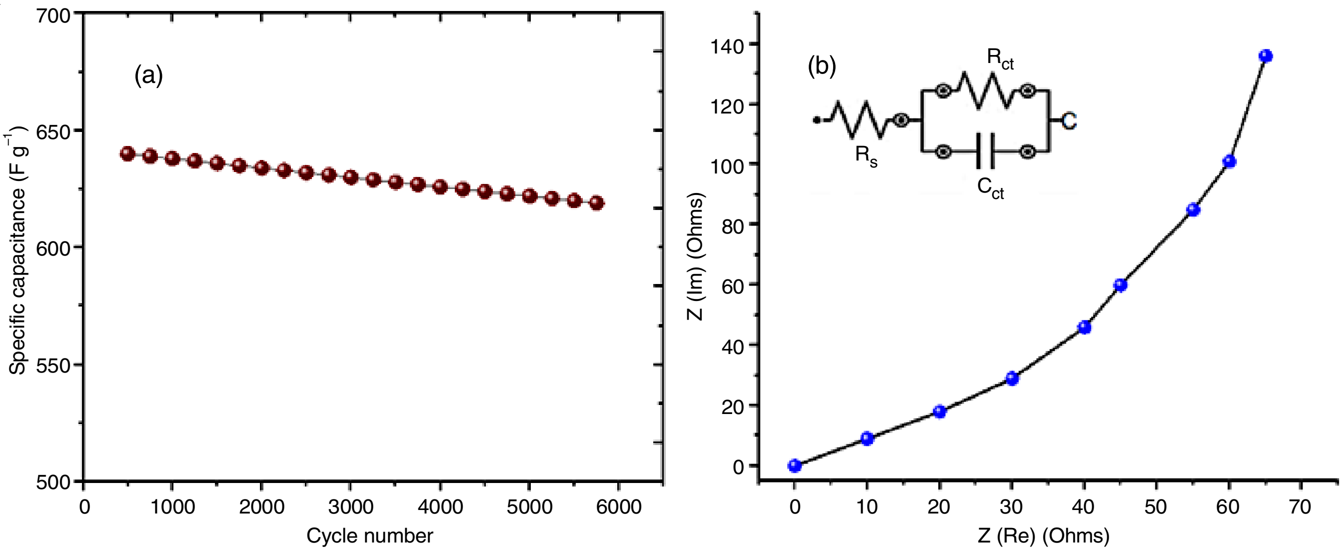


Fig. 6. Cycle stability study (a) and EIS (b) analysis results of copper nanoparticles synthesized using onion seed essential oil

Conclusion

This study utilizes a green chemistry approach for the fabrication of copper nanoparticles utilizing essential oil extracted from onion seed with ~ 17.6 nm as particles average size. The nanoparticles formed by the involvement of essential oil components such as 2-phenylethanol, 1-hexanol, α-phellandrene, 2-pentylfuran, palmitic acid and trimethylbenzene with 80.95% of copper content. The applicability of synthesized nanoparticles as supercapacitor electrodes in energy storage device was studied. The nanoparticles exhibit significantly very high specific capacitance of 364 F/g with 98.7% retention capacity at 1 A/g current density. These nanoparticles exhibit the cyclic stability of 97.1% after 6000 charge/discharge cycles. The enhanced electrochemical efficiency of synthesized nanoparticles was due to the presence of large number of active sites in the formed nanoparticles that facilitates the effective charge transfer. The findings conclusively demonstrated that the nanoparticle synthesized through green method has cost-efficient and effective solution as energy storage in future energy devices.

CONFLICT OF INTEREST

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

REFERENCES

1. N. Kumar, S.-B. Kim, S.-Y. Lee and S.-J. Park, *Nanomaterials*, **12**, 3708 (2022); https://doi.org/10.3390/nano12203708
2. A.R. Bagheri, N. Aramesh, M.S. Hasnain, A.K. Nayak and R.S. Varma, *Chem. Phys. Impact*, **7**, 100255 (2023); https://doi.org/10.1016/j.chphi.2023.100255
3. S. Khasim, A. Pasha, S.G. Dastager, C. Panneerselvam, T.A. Hamdalla, S.A. Al-Ghamdi, S. Alfadhli, M.B. Makandar, J.B. Albalawi and A.A. Darwish, *Ceram. Int.*, **49**, 20688 (2023); https://doi.org/10.1016/j.ceramint.2023.03.200
4. V.V. Makarov, A.J. Love, O.V. Sinitsyna, S.S. Makarova, I.V. Yaminsky, M.E. Taliansky and N.O. Kalinina, *Acta Nat.*, **6**, 35 (2014); https://doi.org/10.32607/20758251-2014-6-1-35-44
5. D. Gupta, A. Boora, A. Thakur and T.K. Gupta, *Environ. Res.*, **231**, 116316 (2023); https://doi.org/10.1016/j.envres.2023.116316
6. G. Marslin, K. Siram, Q. Maqbool, R.K. Selvakesavan, D. Kruszka, P. Kachlicki and G. Franklin, *Materials*, **11**, 940 (2018); https://doi.org/10.3390/ma11060940
7. R.V. Bhupatiraju, B.S. Kumar, P. Peddi and V.S. Tangeti, *J. Chem. Metrol.*, **17**, 181 (2023); https://doi.org/10.25135/jcm.98.2311.2975
8. R.B. Varma and B.S. Rao, *Res. J. Pharm. Technol.*, **15**, 5158 (2022); https://doi.org/10.52711/0974-360X.2022.00868
9. F. Kianian, N. Marefati, M. Boskabady, S.Z. Ghasemi and M.H. Boskabady, *Iran. J. Pharm. Res.*, **20**, 107 (2021); https://doi.org/10.22037/ijpr.2020.112781.13946

10. A. Galavi, H. Hosseinzadeh and B.M. Razavi, *Iran. J. Basic Med. Sci.*, **24**, 3 (2021); https://doi.org/10.22038/ijbms.2020.46956.10843
11. N.A. Sagar, S. Pareek, N. Benkeblia and J. Xiao, *Food Sci. Nutr.*, **3**, 380 (2022); https://doi.org/10.1002/fft2.135
12. B.H.R. Varma and B.S. Rao, *Res. J. Chem. Environ.*, **27**, 54 (2023); https://doi.org/10.25303/2702rjce054061
13. M. Nishimura, T. Muro, M. Kobori and J. Nishihira, *Nutrients*, **12**, 91 (2019); https://doi.org/10.3390/nu12010091
14. R.V. Bhupatiraju, S.R. Battula, M.V.N.R. Kapavarapu and V.R. Mandapati, *Ann. Pharm. Fr.*, **81**, 64 (2023); https://doi.org/10.1016/j.pharma.2022.06.012
15. Y. Wang, Q. Li, X. Peng, Z. Li, J. Xiang, Y. Chen, K. Hao, S. Wang, D. Nie, Y. Cui, F. Lv, Y. Wang, W. Wu, D. Guo and H. Si, *Front. Bioeng. Biotechnol.*, **10**, 856651 (2022); https://doi.org/10.3389/fbioe.2022.856651
16. K.O. Saygi, B. Kacmaz and S. Gul, *Dig. J. Nanomater. Biostruct.*, **16**, 1527 (2021); https://doi.org/10.15251/DJNB.2021.164.1527
17. H. Veisi, N. Dadres, P. Mohammadi and S. Hemmati, *Mater. Sci. Eng. C*, **105**, 110031 (2019); https://doi.org/10.1016/j.msec.2019.110031
18. M.H. Moosavy, M. de la Guardia, A. Mokhtarzadeh, S.A. Khatibi, N. Hosseinzadeh and N. Hajipour, *Sci. Rep.*, **13**, 7230 (2023); https://doi.org/10.1038/s41598-023-33632-y
19. M.V. de Oliveira Brisola Maciel, A. da Rosa Almeida, M.H. Machado, W.C. Elias, C.G. da Rosa, G.L. Teixeira, C.M. Noronha, F.C. Bertoldi, M.R. Nunes, R.D. de Armas and P.L. Manique Barreto, *Biocatal. Agric. Biotechnol.*, **28**, 101746 (2020); https://doi.org/10.1016/j.bcab.2020.101746
20. S. Pervaiz, I. Bibi, W. Rehman, H.F. Alotaibi, A.J. Obaidullah, L. Rasheed and M. M. Alanazi, *Antibiotics*, **12**, 1090 (2023); https://doi.org/10.3390/antibiotics12071090
21. Z. Zakeri, A. Allafchian, M.R. Vahabi and S.A.H. Jalali, *Micro Nano Lett.*, **16**, 533 (2021); https://doi.org/10.1049/mna2.12082
22. R.D. Abdul Jalill, *IET Nanobiotechnol.*, **12**, 678 (2018); https://doi.org/10.1049/iet-nbt.2017.0139
23. S. Ahmadi, M. Fazilati, H. Nazem and S.M. Mousavi, *Biomed. Res. Int.*, **2021**, 8822645 (2021); https://doi.org/10.1155/2021/8822645
24. M. Rashidipour, S. Soroush, B. Ashrafi, A. Sepahvand, B. Rasoulian, S.S. Sohrabi and E. Babaeenezhad, *Biologia*, **79**, 333 (2023); https://doi.org/10.1007/s11756-023-01555-8
25. D. Pathania, S. Kumar, P. Thakur, V. Chaudhary, A. Kaushik, R.S. Varma, H. Furukawa, M. Sharma and A. Khosla, *Sci. Rep.*, **12**, 11431 (2022); https://doi.org/10.1038/s41598-022-14984-3
26. L. Dorjee, R. Gogoi, D. Kamil, R. Kumar, T.K. Mondal, S. Pattanayak and B. Gurung, *Front. Microbiol.*, **14**, 1204512 (2023); https://doi.org/10.3389/fmicb.2023.1204512
27. S. Rajkumar, E. Elanthamilan, S.-F. Wang, H. Chryso, P.V.D. Balan and J.P. Merlin, *Resour. Conserv. Recycling*, **180**, 106180 (2022); https://doi.org/10.1016/j.resconrec.2022.106180
28. I.L. Ikhioya, E.U. Onoh, A.C. Nkele, B.C. Abor, B. Obitte, M. Maaza and F.I. Ezema, *East. Eur. J. Phys.*, **1**, 162 (2023); https://doi.org/10.26565/2312-4334-2023-1-20
29. P.M.Y. Ansari, R.M. Muthukrishnan, R.I. Khan, K. Sakthipandi, C. Vedhi and S.M. Abdul Kader, *Chem. Phys. Impact.*, **7**, 100374 (2023); https://doi.org/10.1016/j.chphi.2023.100374
30. M.A. Alsharif, A. Alatawi, T.A. Hamdalla, S. Alfadhli and A.A.A. Darwish, *Sci. Rep.*, **13**, 22321 (2023); https://doi.org/10.1038/s41598-023-49760-4
31. J. Meena, N. Kumaraguru, N.S. Veerappa, J. Tatsugi, A.S. Kumar, P. Shin and K. Santhakumar, *Sci. Rep.*, **13**, 22499 (2023); https://doi.org/10.1038/s41598-023-49706-w
32. S.C. Mali, A. Dhaka, S. Sharma and R. Trivedi, *Inorg. Chem. Commun.*, **25**, 110448 (2023); https://doi.org/10.1016/j.inoche.2023.110448
33. J.S. Kumar, M. Jana, P. Khanra, P. Samanta, H. Koo, N.C. Murmu and T. Kuila, *Electrochim. Acta*, **193**, 104 (2016); https://doi.org/10.1016/j.electacta.2016.02.069
34. A.M. Alturki Benign, *Biomass Convers. Biorefin.*, **18**, 1 (2022); https://doi.org/10.1007/s13399-022-03303-5
35. S. Ravichandran, J. Radhakrishnan, P. Sengodan and R. Rajendran, *J. Mater. Sci. Mater. Electron.*, **33**, 9403 (2022); https://doi.org/10.1007/s10854-021-07340-0
36. H.E. Nsude, K.U. Nsude, G.M. Whyte, R.M. Obodo, C. Iroegbu, M. Maaza and F.I. Ezema, *J. Nanopart. Res.*, **22**, 352 (2022); https://doi.org/10.1007/s11051-020-05071-7
37. R. Teimuri-Mofrad, R. Hadi, H. Abbasi, E. Payami and S. Neshad, *J. Organomet. Chem.*, **899**, 120915 (2019); https://doi.org/10.1016/j.jorganchem.2019.120915
38. S. Yadav, N. Rani and K. Saini, *Mater. Today Proc.*, **49**, 2124 (2022); https://doi.org/10.1016/j.matpr.2021.08.323
39. Y.N. Sudhakar, H. Hemant, S.S. Nitinkumar, P. Poornesh and M. Selvakumar, *Ionics*, **23**, 1267 (2017); https://doi.org/10.1007/s11581-016-1923-7