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Synthesis of Zinc Oxide Nanoparticles and Setariaverticillata Assisted Activated Carbon Blended Zinc Oxide Nanoparticles

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Abstract

Objectives: In this work *Setariaverticillata* leaf extract was utilized as bioreductant to synthesise Zinc oxide nanoparticles (ZnO-NPs) blended with activated carbon for possible application in electrochemical energy conversion systems. **Methods/ Statistical Analysis**: Synthesised ZnO-NPs were subjected to various physical characterization techniques. As well as the electrochemical behaviour of the *Setariaverticillata* activated carbon (SVAC) and nanostructured ZnO composite mixture was studied electrochemical impedance spectroscopy with 0.1 M Na_2SO_4 electrolyte. **Findings:** Wurtzite (hexagonal) form of the herb assisted synthesised ZnO-NPs with particles disseminated within the extend of 40-110 nm. The prepared AC-ZnOnanocomposite electrode exhibits specific capacitance of 264.8 F/cm^2 at 5 mV/s scan rate. The specific capacitance of the electrodes diminished with increment in zinc oxide substance. The improved electrochemical behaviour of the nanocomposite can be credited to the high electrical conductivity of the activated carbon and electro active. **Application/ Improvements:** ZnO *Setaria* assisted activated carbon-ZnOnanocomposite was prepared as a perspective candidate to exhibit its applicability as active materials for electrochemical energy conversion such as super capacitors.

Keywords: AC-ZnOnanocomposite, Nanomaterial, Supercapacitor, Specific Conductance, ZnO

1. Introduction

Nanotechnology is developed as a modern field of research dealing with synthesis of nanoparticles and their applications in different areas such as photocatalysis, biomedicines, electrochemistry, sensors, pharmaceutics, well being care, beauty care products, nourishment innovation, textile industry, energy science, optical devices, etc[1–3]. Surface morphology of the nanoparticles plays a crucial part in different applications. Semiconductor nanoparticles has gained attention in the current scenario because they have better possibilities in optoelectronics and bioapplications[4,5]. Among the various semiconductor nanoparticles, ZnO has received considerable attention because of its unique property of having high excitation binding energy of 60 meV[6] and band gap of 3.3 eV[7]. ZnO-NPs are being synthesised throughvarious physical and chemical methods which includes wet chemical route[8], vapour phase process[9], hydrothermal[10], precipitation[11] sonochemical methods etc. However,these methods involvethe usage of toxic chemicals, expensive instruments and tedious process. Therefore, development of inexpensive and green strategy to synthesis ZnO-NPs is really demanding. Bio-inspired ZnO-NPs has pulled in significant consideration due to its effortlessness, inexpensive and non-toxicity. Demand for simple and secure green strategy in scale up and mechanical production of well scattered metal nanoparticles, plant extracts are considered as amazing availablebioresource[12–14].

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Due to the restricted accessibility of fossil fuel and its associated drawbacks of worldwide warming and natural contamination. Current research focuses on the development of renewable energy resources along with eco-friendly technology for energy conversion and storage[15,16]. Supercapacitors are also known as electrochemical capacitors which finds wide applications because of high power density, natural invitingness, long life time and long shelf life[17,18]. Much of the research has been carried out to increase the overall performance of the super capacitors. ZnO is an important battery active material with the battery density of 650A/g, eco-friendly in nature and promising electrode for super capacitorapplications[19]. In this work, bioinspired ZnO-NPswas synthesized utilizing *Setariaverticillate* as bioreductant. Activated carbon-ZnOnanocomposite electrode has been prepared as a potential candidate for fabrication of super capacitors and electrochemical properties was evaluated by using electrochemical impedance spectroscopy.

2. Experimental

2.1 Preparation of Setariaverticillata Leaf Extract (SVLE)

Setariaverticillata leaves were gathered and utilized for the preparation of aqueous leaf extract of *Setariaverticillata.* The collected leaves were washed well with deionised water and remove grime particles and then chop into small pieces.The freshly chop leaf pieces (40g) was boiled with 400 ml deionized water and boiled at 90°C for 0.17 hour.The obtained crude extract was cooled in well-ventilated area (approximately 28°C), filtered through Whatmann filter and refrigerated for further use.

2.2 Eco-Friendly Synthesis of Zinc Oxide Nanoparticles

The white, crystalline Zinc nitrate was acquired from S.D.Fine chemicals (Bangalore, India). The fresh herb extract was added with 10 mM $Zn(NO_3)_2$ solution in a RB flask at ambient temperature for 6 h. The pale-yellow colour solution thus obtained was dried at 100°C in hot-air oven. The resultant mass obtained was subjected to calcination at 400 °C to get fine solid of ZnO-NPs and kept in air free containers. Green approach of formation of *Setaria* mediated ZnO-NPs is shown in Figure 1.

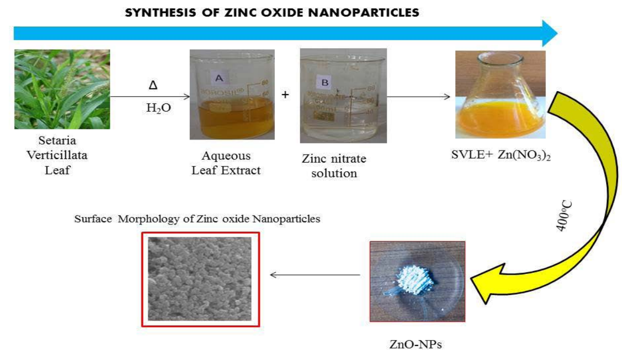

Figure 1. Schematic synthetic route of Zinc oxide nanoparticles.

2.3 Preparation of Setariaverticillata Activated Carbon (SVAC)

*Setariaverticillata*leaves were first washed a few times with demineralized water to expelresidue, soil and suspended impurities. The material is grounded by using pestle and mortar to turn it into fineparticles. About 100g of powdered fine materials was blended with 0.05 L of conc. H_2SO_4 and kept at room temperature for 24 h. Then washed with double distilled water to remove excess of acid and dried at 110 °C for 14h to remove moisture and stored in dry atmosphere.

2.4 Preparation of AC-ZnO Electrode

Activated carbon was blended with ZnO in three distinct proportions {2:0.5, 2:3, 2:2, 2:1} by utilizing n-methyl pyrrolidone along with binding agent, polyvinylidiene fluoride and made into a paste. After that, the paste AC-ZnO composite was applied with a brush on weighed stainless steel current collector and dried at 25 °C.

2.5 Electrochemical Characterisation of Electrode

Electrochemical impedance measurements were performedin 0.01 L of 100mM Na_2SO_4 electrolyte over a potential range of -0.9 V to + 0.1 V, the solution was employed as the experimental solution for ZnO nanoparticles. Electrochemical Impedance Spectroscopy (EIS) of the nanoparticle modified electrodes was measured in 100 mM Na_2SO_4 at perturbation amplitude of 0.01 V within a frequency range of 0.0001 mHz to 100 mHz.

2.6 Characterisation of Setaria Mediated ZnO-NPs

UV-1601 Shimadzu spectrophotometer is utilized to record UV-Vis spectra which were confirmed the formation of ZnO-NPs. Functional groups of *Setaria verticillata* and bio synthesised ZnO-NPs analysed by FT-IR spectra with the help of BRUKER-FTIR-TENSOR-27 spectrophotometer instrument. The size, shape and elemental composition of bio-synthesised ZnO-NPs were investigated by using SEM, Hitachi S4700, equipped with Energy Dispersive Spectroscopy (EDS). The phase identification of bio-synthesised ZnO-NPs analyzed with X-ray diffractometer (PANanalytical X-Pert PRO).

3. Results and Discussion

3.1 Characterization of Bio-Synthesised ZnO-NPs

UV–Vis spectral technique is an important role in anticipating the formation of metal oxide nanoparticles. Absorption spectrum of the *Setaria verticillata* leaf extract, *Setaria verticillata* associated with Zinc Nitrate and biosynthesized ZnO nanoparticles is depicted in Figure 2.

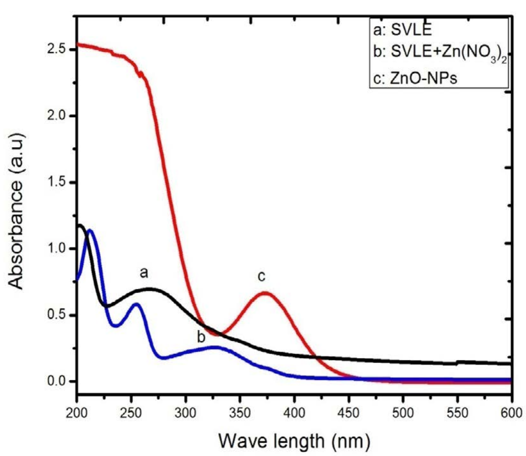

Figure 2. (a) The UV-visible spectrum of *Setariaverticillata* leaf extract. (b) *Setariaverticillata* leaf extract with zinc nitrate. (c) ZnO-NPs.

From the figure, it is confirmed that Surface Plasmon Resonance (SPR) band for ZnO nanoparticles due to the absorption peak occurred at 376 nm[20]. This is inagreement with the reported work on the eco-friendly synthesis of ZnO-NPs (absorption peak at 374 nm) utilizing various herb extracts[21,22], which affirmed the presence of ZnO nanoparticles.

Figure 3(a), (b), FT-IR spectra of the *Setariaverticillata* leaf extract and synthesised ZnO-NPs. FT-IR spectra of the *Setariaverticillata* spectra reveals many absorption peaks at 1060, 1402, 1625, 2350,2926, 3400 cm^{-1} together with other tiny peaks. These bands relate to C-H bending modes within the organic compound chains, C-H bend of alkynes and C-O stretching, C-OH stretching vibrations, C=C stretching, C=O group,– OH and/or –NH stretching vibrations. A wide peak due to –OH band is observed at 3450 cm^{-1}. A weak absorption peaks at 2922 cm^{-1} and 2852 cm^{-1}are due to aliphatic asymmetric C-H stretching vibrations and carboxylic acids stretching –C-H. The peak at 1745 cm^{-1} corresponds to C=O stretching vibrations of carbonyl group. The weak absorptionpeaks at 1164 cm^{-1} and 1322 cm^{-1} are indicative of C=N stretching of amide bonds. In addition, C-O-C stretching vibrationscoincide with the absorption peak at 1020 cm^{-1}. The crest at 744 cm^{-1} is due to existence of R-CH group and peak at 669 cm^{-1} demonstrates the vibration band of ZnO-NPs according to the data recordeddistinctivepeak at 490 cm^{-1} can be ascribed to the [Zn-O] bond of metal oxygen[23,24].

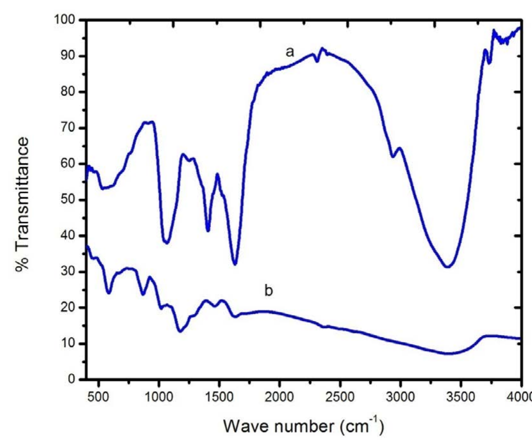

Figure 3. (a) The FT-IR spectrum of SVLE. (b) SetariamediatedZnO-NPs.

Figure 4(a) indicates that synthesised ZnO-NPs have ball shape and particle dimension varies between 40-110 nm.The EDX spectrum of eco-friendly synthesised ZnO-NPs as displayed in Figure 4(c) reveals the chemical characterization of ZnO-NPs and high purity of ZnO-NPs except impurities. Scanning electron microscopy was used to assign the shape, size and morphology of activated carbon prepared from *Setariaverticillata* leaves (Figure 4(b)). Figure 4(b) confirms the particle size in the range of 8-10 nm.Further confirmation of prepared activated carbon was done by Energy Dispersive X-ray analysis (EDX). Figure 4(d) for the activated carbon showed two characteristic signals for C and O composition as 73.52%, 26.48% respectively.

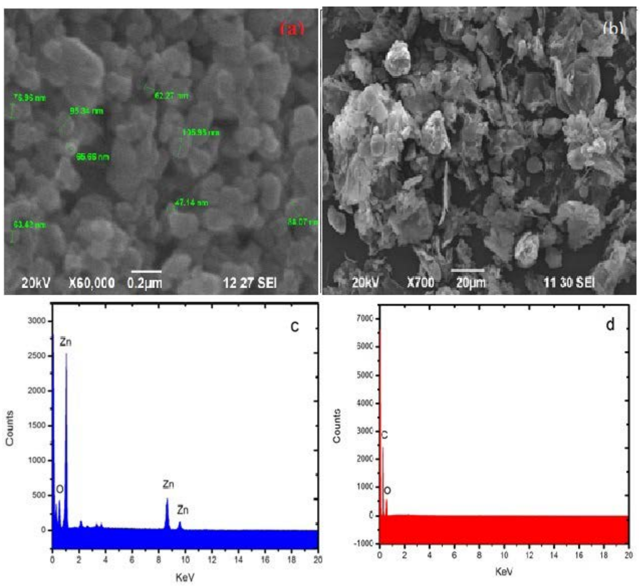

Figure 4. (a) SEM image of ZnO-NPs. (b) SEM image of Activated carbon prepared from Setariaverticillata Leaves. (c) EDX spectra of pure ZnO-NPs. (d) EDX spectra of activated carbon.

The XRD analysis of the *Setaria* mediated Zinc oxide nanoparticles reveals the chemical composition, physical properties and crystallographic structure of the ZnO-NPs (Figure 5(a)).The obtained diffraction peaks at 31.9, 34.8, 36.8, 47.5, 56.3, 62.9, 68.1, 69.2 and 77.0 as shown in Figure 5(a) corresponds to miller indices of 100, 002, 10 1, 102, 110, 103, 112, 201and 202 planes respectively. The got outcomes were in appropriate agreement with JCPDS file No. 036-1451 confirming the hexagonal wurtzite structure[25]. The clear severe peak bought suggests the excessive purity and crystalline nature of the synthesised ZnO-NPs. No differentdiffraction peaks are recognized suggesting purity of the synthesized ZnO-NPs. Figure 5(b) displays XRD pattern of activated carbon. The characteristics 10-30º peaks of SVAC were discernible in carbon, the obtained diffraction spectrum did not show any obvious peak at the scan range 10-90º thereby indicating the amorphous phase of SVAC.

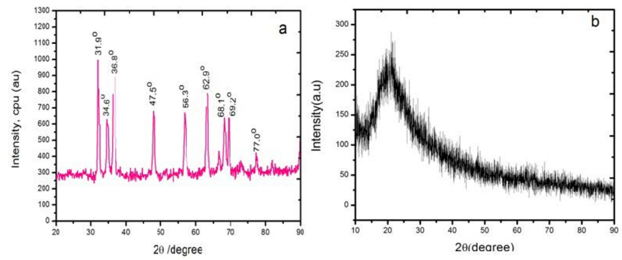

Figure 5. (a) XRD patterns of SetariamediatedZnO-NPs. (b) XRD spectrum of activated carbon.

3.2 Electrochemical Properties of AC-ZnO Composite and Supercapacitors

AC-ZnOnanocomposite electrodes was prepared with various composition ratios such as 2:0.5, 2:1, 2:2 and 2:3 prepared on stainless steel panels. Figure 6 shows the Nyquistplots for the AC-ZnOnanocomposite having different compositions in the ratios 2:1, 2:2 and 2:3. The specific capacitance calculation shows that composite composition in the ratio 2:0.5 has highest specific conductance as shown in Table 1. Figure 7 shows the Nyquist plot for nanocomposite electrode with 2:0.5 composition which exhibits lowest resistance and higher specific capacitance. The improved electrochemical performance of AC-ZnOnanocomposite can be attributed to the electro active property of ZnOsupported on activated carbon provides a three-dimensional conducting system which givesactive sites for the formation of electrical double layer[26] and pseudo capacitance from the ZnO provides a higher specific capacitance[27,28].

Table 1. Electrochemical Impedance parameters for AC-ZnO electrode in 0.1 M Na_2SO_4

Materials	Scan rate (mV/Sec)	Charge transfer resistance (cm^2)	Capacitance (F/cm^2)
AC-ZnO (2:3)	5	4.1	2.5
AC-ZnO (2:2)	5	40.3	30.5
AC-ZnO (2:1)	5	59.2	57.4
AC-ZnO (2:0.5)	5	1602.0	264.8

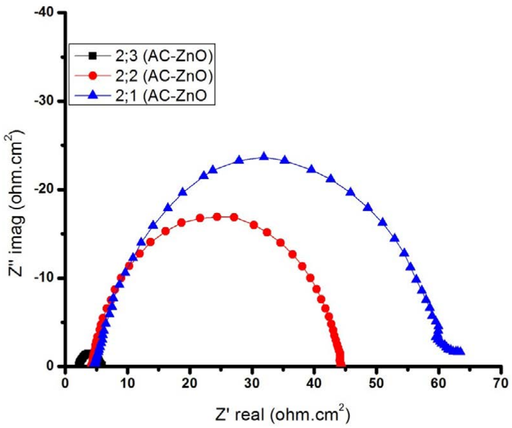

Figure 6. Impedance plots for AC-ZnO composites at compositions of 2:3, 2:2 and 2:1.

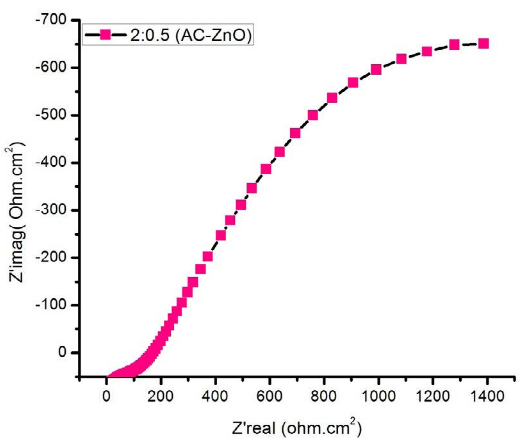

Figure 7. Impedance plots for AC-ZnO composites at 2:0.5 mass ratio.

4. Conclusion

In the present work, we report the nanostructured ZnO has been prepared by using *Setariaverticillata* as bioreductant. Biosynthesised ZnO-NPs acted as super capacitor by using composting with activated carbon. Super capacitor was fabricated by using the composite electrodes and studied for electrochemical properties using electrochemical impedance spectroscopy. The studies reveal that super capacitor has good capacitance and can be used as a super capacitor active material.

5. References

1. Huanga NM, Limb HN, Radimanc S, Khiewd PS, Chiud WS, Hashime R, Chiac CH. Sucrose ester micellar-mediated synthesis of Ag nanoparticles and the antibacterial properties. Colloids and Surfaces A: Physicochemical and Engineering Aspects. 2010; 353:69-76. https://doi.org/10.1016/j.colsurfa.2009.10.023
2. Nel A, Xia T, Madler L, Li N. Toxic potential of materials at the nanolevel. Science. 2006; 311:622-7. https://doi.org/10.1126/science.1114397 PMid:16456071
3. Amornpitoksuk P, Suwanboon S, Sangkanu S, Sukhoom A, Wudtipan J, Srijan K, Kaewtaro S. Synthesis, photocatalytic and antibacterial activities of ZnO particles modified by diblock copolymer. Powder Technology. 2011; 212:432-8. https://doi.org/10.1016/j.powtec.2011.06.028
4. Konenkamp R, Dloczik L, Ernst K, Olecsh C. Nanostructures for solar cells with extremely thin absorbers. Physica E: Low-dimensional systems and Nanostructures. 2002; 14:219-23. https://doi.org/10.1016/S1386-9477(02)00387-9
5. Vayssieres L, Keis K, Hagfeldt A, Lindquist SE. Three dimensional array of highly oriented crystalline ZnOMicrotubes. Chemistry of Materials. 2001; 13:4395-8. https://doi.org/10.1021/cm011160s
6. Yilmaz S, Nisar J, Atasoy Y, McGlynn E, Ahuja R, Paralak, Bacaksiz E, Defect induced room temperature ferromagnetism in B-doped ZnO. Ceramics International. 2013; 39:4609-17. https://doi.org/10.1016/j.ceramint.2012.11.060
7. Suwanboon S, Amornpitoksuk P, Sukolrat A, Muensit N. Optical and photocatalytic properties of La-doped ZnO nanoparticles prepared via precipitation and mechanical milling method. Ceramics International. 2013; 39:2811-9. https://doi.org/10.1016/j.ceramint.2012.09.050
8. Taunk PB, Das R, Bisen DP, Tamrakar RK. Structural characterization and photoluminescence properties of zinc oxide nano particles synthesized by chemical route method. Journal of Radiation Research and Applied Sciences. 2015; 8:433-8. https://doi.org/10.1016/j.jrras.2015.03.006
9. Kolekar TV, Bandgar SS, Shirguppikar SS, Ganachari VS. Synthesis and characterization of ZnO nanoparticles for efficient gas sensors. Archives of Applied Science Research. 2013; 5:20-8.
10. Balantrapu K, Goia D. Silver nanoparticles for printable electronics and biological applications. Journal of Materials Research. 2009; 24:2828-36. https://doi.org/10.1557/jmr.2009.0336
11. Tripathi RM, Saxena A, Gupta N, Kapoor H, Singh RP. High antibacterial activity of silver nanoballs against E.

coli MTCC 1302, *S. typhimurium*, MTCC 1254, *B. subtilis* MTCC 1133 and *P. aeruginosa* MTCC 229. Digest Journal of Nanomaterials and Biostructures. 2010; 5:323-30.

12. Sundrarajan M, Ambika S, Bharathi K. Plant-extract mediated synthesis of ZnO nanoparticles using *Pongamiapinnata* and their activity against pathogenic bacteria. Advanced Powder Technology. 2015; 26:1294-99. https://doi.org/10.1016/j.apt.2015.07.001
13. Jeevanandam J, Chan YS, Danquah MK. Biosynthesis of metal and metal oxide nanoparticles. ChemBioEng Reviews. 2016; 3:55-67. https://doi.org/10.1002/cben.201500018
14. ShankerU, Jassal V, Rani M, Kaith BS. Towards green synthesis of nanoparticles, from bio-assisted sources to benign solvents. A review. International Journal of Environmental Analytical Chemistry. 2016; 96:801-35.
15. Wang G, Zhang L, Zhang J. A review of electrode materials for electrochemical Super capacitors. Chemical Society Reviews. 2012; 41:797-828. https://doi.org/10.1039/C1CS15060J PMid:21779609
16. Bose S, Kuila T, Mishra AK, Rajasekar R, Kim NH, Lee JH. Carbon based Nanostructured materials and their composites as super-capacitor electrodes. Journal of Materials Chemistry. 2012; 22:767-84. https://doi.org/10.1039/C1JM14468E
17. Wang J, Gao Z, Li Z, Wang B, Yan Y, Liu Q, Mann T, Zhang M, Jiang Z. Green synthesis of grapheme nano sheets/ZnO composites and electrochemical properties. Journal of Solid State Chemistry. 2011; 184:1421-7. https://doi.org/10.1016/j.jssc.2011.03.006
18. Baker J. New technology and possible advances in energy storage. Energy Policy. 2008; 36:4368-73. https://doi.org/10.1016/j.enpol.2008.09.040
19. Selvakumar M, Bhat DK, Aggarwal AM, Iyer SP, Sravani G. Nano ZnO-activated carbon composite electrodes for super capacitors. Physica B. 2010; 405:2286-9. https://doi.org/10.1016/j.physb.2010.02.028
20. Kanagamani K, Muthukrishnan P, Saravanakumar K, Shankar K, Kathiresan A, Photocatalytic degradation of environmental perilous gentian violet dye using *Leucaena*-mediated zinc oxide nanoparticle and its anticancer activity. Rare metals. 2019; 38:277-86. https://doi.org/10.1007/s12598-018-1189-5
21. Bhuyan T, MishraK, Khanuja M, Prasad R, Varma A. Biosynthesis of zinc oxide nanoparticles from *Azadirachtaindica* for antibacterial and photocatalytic applications. Materials Science in Semiconductor Processing. 2015; 32:55-61. https://doi.org/10.1016/j.mssp.2014.12.053
22. Sangeethaa G, Rajeshwari S, Venckatesh R. Green synthesis of zinc oxide nanoparticles by aloebarbadensis miller leaf extract Structure and optical properties. Mater Res Bull. 2011; 46:2560-6. https://doi.org/10.1016/j.materresbull.2011.07.046
23. Abdul Salam H, Sivaraj R, Venckatesh R. Green synthesis and characterization of zinc oxide nanoparticles from *Ocimumbasilicum* L. var. *purpurascens* Benth.-Lamiaceae leaf extract. Materials Letters. 2014; 131:16-8. https://doi.org/10.1016/j.matlet.2014.05.033
24. Azizia S, Ahmada MB, Namvarb F, Mohama R, Green biosynthesis and characterization of zinc oxide nanoparticles using brown marine macroalga *Sargassummuticum* aqueous extract. Materials Letters. 2014; 116:275-7. https://doi.org/10.1016/j.matlet.2013.11.038
25. Vanathi P, Rajiv P, Narendhran S, Rajeshwari S, Rahman PKSM, Venckatesh R. Biosynthesis and characterization of phytomediated zinc oxidenanoparticles- A green chemistry approach. Materials Letters. 2014; 134:13-5. https://doi.org/10.1016/j.matlet.2014.07.029
26. Li Z, Liu P, Yun G, Shi K, Lv X, Li K, Xing J, Yang B. 3D (Three dimensional) sandwich structured of ZnO (zinc oxide)/rGO (reduced grapheme oxide)/ZnO for high Performance supercapacitors. Energy. 2014; 69:266-71. https://doi.org/10.1016/j.energy.2014.03.003
27. Hsieh CT, Lin JS, Chen YF, Lin CY, Li WY. Graphene sheets anchored with ZnO nanocrystals as electrode materials for electrochemical capacitors. Materials Chemistry and Physics. 2014; 143:853-9. https://doi.org/10.1016/j.matchemphys.2013.10.024
28. Zhang Y, Li H, Pan L, Lu T,Sun Z. Capacitive behaviour of grapheme-ZnO composite film for supercapacitors. Journal of Electroanalytical Chemistry. 2009; 634:68-71. https://doi.org/10.1016/j.jelechem.2009.07.010