Supercapacitor Properties of Green Synthesised Zinc Oxide Nanoparticles by Using Setaria Verticillata Extract

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The biological reducing agents are more important since they lessen the negative effects of the dangerous chemicals used to create nanoparticles. The experimental work uses a bio-reductant free method for producing zinc oxide nanoparticles using an aqueous leaf extract of Setaria verticillata. Scanning electron microscopy (SEM) tests confirmed that the Wurtzite appearance of the herb helped synthesise ZnO-NPs through particles dispersed inside the range of 40–110 nm. Nanostructured ZnO composite and Setaria verticillata activated carbon were used to create a symmetrical super capacitor. Using 0.1 M Na2SO4 as the electrolyte, electrochemical impedance spectroscopy was used to organise the nanocomposite anodes into super capacitors. At a inspect speed of 5 mV/s, the generated AC-ZnO nanocomposite electrode displays precise capacitance of 264.8 F/cm2. With an increase in zinc oxide content, the electrodes specific capacitance decreased. The higher electrical conductivity of the electroactive ZnO and activated carbon is responsible for the nanocomposites improved electrochemical performance.
Keywords: ZnO, AC-ZnO nanocomposite, Super capacitor, Specific conductance.

1. Introduction

Synthesis of nanoparticles and their applications in various fields, including photocatalysis, biomedicines, electrochemistry, sensors, energy science, optical devices, etc., have led to the development of nanotechnology as a contemporary field of study [1-3]. In many applications, the surface morphology of the nanoparticles is important. In the contemporary context, semiconductor nanoparticles have garnered interest due to their superior potential in optoelectronics and bioapplications [4-5]. ZnO is one of the different types of semiconductor nanoparticles that have drawn a lot of interest due to its special characteristics, which include a band gap of 3.3 eV [6] and a high excitation required power of 60 meV [7]. Numerous physical and chemical techniques, such as the wet chemical approach [8], the steam phase procedure [9], the hydrothermal [10], the precipitation [11], the sonochemical method, etc., are being used to synthesise ZnO-NPs. Nevertheless, these techniques require the use of costly equipment, hazardous chemicals, and laborious procedures. Thus, the development of a simple and environmentally friendly method for synthesising ZnO-NPs is imperative. Because bio-inspired ZnO-NPs are simple, affordable, and non-toxic, they have attracted a lot of attention.

Plant extracts are regarded as an incredible readily available bioresource due to the demand for a straightforward and safe green method in the mechanical and scale-up manufacturing of well-dispersed metal nanoparticles [12–14] due to the limited availability of fossil fuels and the problems they cause, such as global warming and environmental damage. The development of sustainable energy resources and environmentally friendly energy conversion and storage technologies is the main focus of current research [15–16]. Super capacitors are one type of energy storage technology that has advantages over batteries. Supercapacitors, often referred to as electrochemical capacitors, contain widespread series of uses due to their elevated power density, attractive design, extended lifespan, and extended shelf life [17–18]. The difference between batteries and regular capacitors is filled by super capacitors. A significant amount of investigate has been finished to get better the super capacitors taken as a whole performance. With a battery concreteness of 650A/g, zinc oxide (ZnO) is a significant battery active material that is also environmentally acceptable and a promising electrode for super capacitor applications [19]. This work used Setaria verticillata as a bioreductant to synthesise bio-inspired ZnO-NPs. EI spectroscopy was used to assess the electrochemical characteristics of an activated carbon-ZnO nanocomposite electrode, which be developed as possible aspirant for the production of supercapacitors.

2. Materials and Method

2.1. Making extracts from Setaria verticillata leaves

Aqueous Setaria verticillata leaf extract was made using the leaves of the plant that were collected. After thoroughly washing the gathered leaves in deionised water to obtain rid of any dirt, they were chopped into little pieces. Forty grammes of freshly chopped leaf pieces were cooked for 0.17 hours at 90 °C in 400 millilitres of deionized water. The resulting crude extract was filtered using a Whatmann filter, chilled for later use, and allowed to cool to around 28 °C in a well-ventilated location.

2.2 Sustainable production of ZnO nanoparticles

After adding the clean herb extract, a 10 mM $Zn(NO_3)_2$ solution was added and left to sit at space temperature for six hours. The resultant crude extract was dehydrated out at 100 °C in a burning oven. The resulting solution, which had a pale yellow hue, was baked to dryness at 100 °C. The consequential mass was calcinated at 400 °C to produce a well frozen ZnO-NPs, which were then stored in atmosphere tight containers. Figure 1 illustrates the green method of creating ZnO-NPs mediated by Setaria verticillata.

Figure 1. Schematic synthetic route of Zinc oxide nanoparticles.

2.3. Making Activated Carbon from Setaria verticillata

The leaves of Setaria verticillata were first repeatedly cleaned with demineralized water to remove dirt, debris, and suspended pollutants. To crush the substance into fine particles, a pestle and mortar are used. A mixture of roughly 100g of finely powdered materials and 0.05 L of concentrated sulfuric acid was left to stand up at space temperature for a day. To get rid of extra acid, double distilled water was used to wash the dried SVAC. After being dried for 14 hours at 110 °C to eliminate moisture, the material was sealed in a bottle

2.4. Setting up the AC-ZnO electrode

Activated carbon and ZnO were combined using n-methyl pyrrolidone in three different ratios ({2:0.5, 2:3, 2:2, 2:1}) and the binding agent polyvinylidiene fluoride to form a paste. Next, the weighted stainless steel current collector was brushed with the glue AC-ZnO composite, and it was dehydrated at 25 ºC.

2.5. Characterization of the electrode electrochemically

The experimental solution for ZnO nanoparticles was 0.01 L of 100 mM Na_2SO_4 electrolyte, in which electrochemical impedance measurements were carried out in excess of a possible array of -0.9 V to + 0.1 V. The nanoparticle modified electrodes were subjected to electrochemical impedance spectroscopy (EIS) in 100 mM Na_2SO_4 at perturbation amplitude of 0.01 V, covering a frequency of array of 0.0001 mHz to 100 mHz.

2.6. ZnO-NPs mediated by Setaria: characterization

Bruker FT-IR, were acquired at space temperature and used to evaluate the synthesised ligand using infrared spectra (model (SPECTRUM TWO) PERKIN ELMER) (KBr discs) in

4000-400 cm-1. PerkinElmer was used to record UV-Vis and photoluminescence. Using SEM and EDS, the dimensions, form, and elemental makeup of the biosynthesised ZnO-NPs were examined. Using an X-ray diffractometer (PAN analytical X-Pert PRO), the phase identification of biosynthesised ZnO-NPs was examined.

3. Results and Discussion

3.1. Evaluation of ZnO-NPs Produced via Biosynthesis

A vital instrument for predicting the development of metal oxide nanoparticles is the UV-Vis spectral method. Figure 2 shows the incorporation spectrum of the leaf extract and Setaria verticillata linked to zinc nitrate, and bio-synthesized ZnO nanoparticles. The figure confirms that the absorption peak at 376 nm is the reason for the SPR band for ZnO nanoparticles [20]. This contradicts a study that was published [21–22] that confirmed the presence of ZnO nanoparticles through the environmentally friendly manufacture of ZnO-NPs using a variety of herb extracts.

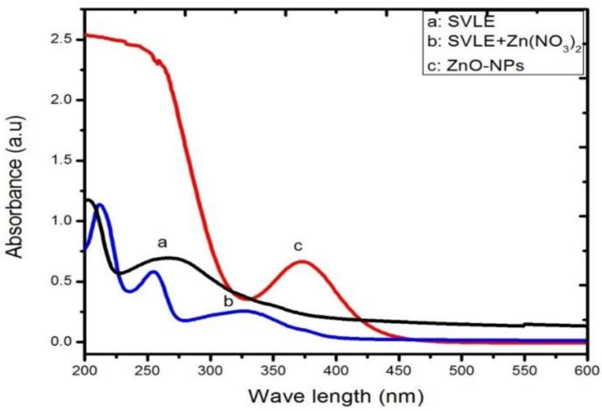

Figure 2. The UV-visible spectrum of Setariaverticillata leaf extract (a),Setariaverticillata leaf extract with zinc nitrate (b) and ZnO-NPs (c)

The FT-IR spectra of the environmentally friendly ZnO-NPs and the leaf extract from Setaria verticillata are shown in Figures 3a and 3b. The Setaria verticillata FT-IR spectra show several incorporation peaks at 1060, 1402, 1625, 2350, 2926, and 3400 cm^{-1} in addition to additional small peaks. These bands are associated with the C-H bending modes found in the chains of organic compounds, the C-H bend of alkynes, the C-O stretching and vibrations, the C=C vibrations and the C=O group, as well as the -OH and/or -NH stretching vibrations. ZnO-NPs vibrational spectra show a broad peak at 3450 that is known as the -OH band. There is a slight absorption for carboxylic acids stretching –C-H and aliphatic asymmetric C-H vibrations at 2922 and 2852 cm^{-1}. The carbonyl group's C=O stretching vibrations are shown by the peak at 1745. The modest absorption peaks at 1164 and 1322 cm^{-1} show that the amide bonds C=N stretching is present. Furthermore, the absorption peak at 1020 is coincident with C-O-C stretching vibrations. According to data obtained, a distinct peak at 490 cm^{-1} can be accredited to the [Zn-O] link of metal oxygen. The crown at 744 cm^{-1} is attributable to the existence of R-CH cluster, and the peak at 669 cm^{-1} shows the shaking band of ZnO-NPs [23–24].

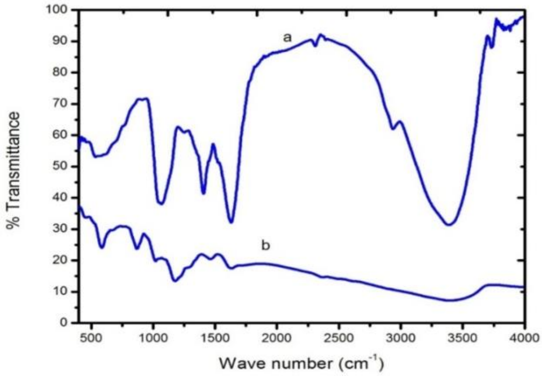

Figure 3. The FT-IR spectrum of SVLE (a) and Setaria mediatedZnO-NPs (b)

Synthesised ZnO-NPs, as shown in Fig. 4a, have a ball form and a particle size range of 40–110 nm. The EDX range of the environmentally responsive ZnO-NPs, as shown in Fig. 4c, shows that the particles are highly pure apart from contaminants and have undergone chemical characterization. The size, form, and morphology of the activated carbon made from Setaria verticillata leaves were identified using scanning electron microscopy (Fig. 4b). The atom size in the 8–10 nm range is confirmed by Fig. 4b. The produced activated carbon was further verified by EDX. Two distinct signals were displayed in Fig. 4d for the activated carbon, with C and O compositions of 73.52% and 26.48%, respectively.

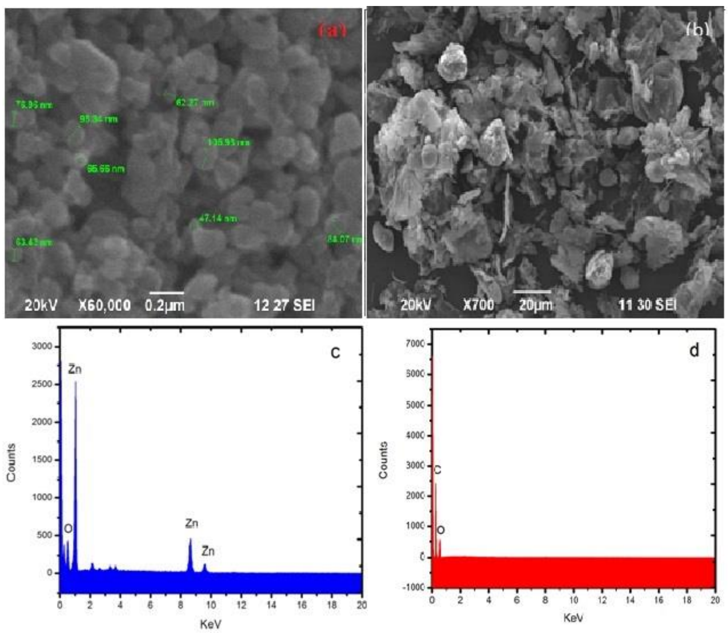

Figure 4. (a) SEM image of ZnO-NPs (b) SEM image of Activated carbon prepared from Setariaverticillata Leaves (c) EDX spectra of pure ZnO-NPs (d) EDX spectra of activated carbon.

The physical characteristics and crystalline structure of the zinc oxide nanoparticles mediated by Setaria are shown by the XRD examination of the ZnO-NPs (Fig. 5a). The diffraction peaks identified in Fig. 5a at 31.9, 34.8, 36.8, 47.5, 56.3, 62.9, 68.1, 69.2, and 77.0 match to miller indices of 100, 002, 101, 102, 110, 103, 112, 201 and 202 planes, in that order. The obtained results validated the hexagonal wurtzite structure and were in proper concurrence with JCPDS file No. 036-1451 [25]. The synthesised ZnO-NPs extreme purity and crystalline nature are suggested by the distinct, sharp peak. There are no discernible distinct diffraction peaks, indicating the synthesised ZnO-NPs purity. The activated carbon XRD pattern is shown in Fig. 5b. Carbon exhibited the classic 10–30º SVAC peaks, but the resulting diffraction spectra showed no clear peak at the scrutinize assortment 10-90º, confirming the amorphous phase of SVAC.

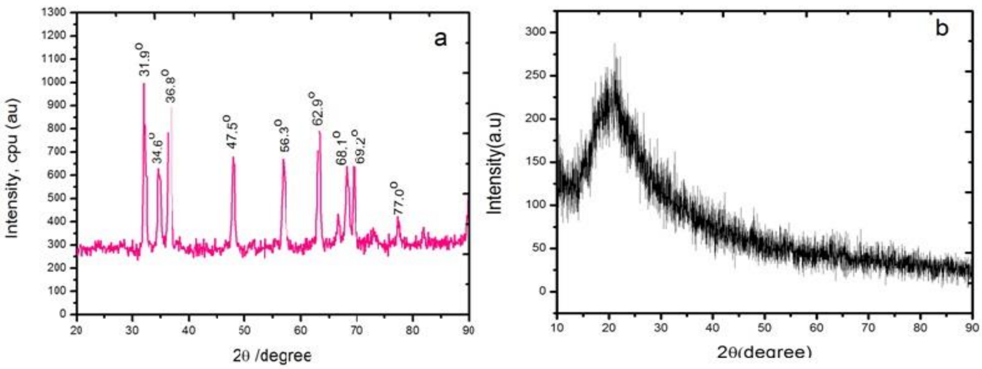

Figure 5. (a) XRD patterns of Setariamediated ZnO-NPs. (b) XRD spectrum of activated carbon.

3.2. The electrochemical characteristics of supercapacitors and AC-ZnO composites

Resting on stainless steel panels, AC-ZnO nanocomposite electrodes with diverse composition ratio such as 2:1, 2:1:3, 2:2, and 2:3 were produced. The Nyquist plots intended for the AC-ZnO nanocomposite with varying compositions in the ratios of 2:1, 2:2, and 2:3 are displayed in Fig. 6. According to Table 1, the composite composition with a ratio of 2:0.5 has the maximum specific conductance, as shown by the specific capacitance calculation. The nanocomposite electrode with a 2:0.5 composition, which has the least possible resistance and the uppermost specific capacitance, is depicted in the Nyquist plot in Figure 7. The electroactive belongings of ZnO supported on activated carbon provide a three-dimensional conducting arrangement that gives energetic sites for the arrangement of an electrical twice coating [26], and pseudo capacitance from the ZnO provide a superior specific capacitance [27–28]. These properties are responsible for the enhanced electrochemical performance of the AC-ZnO nanocomposite.

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

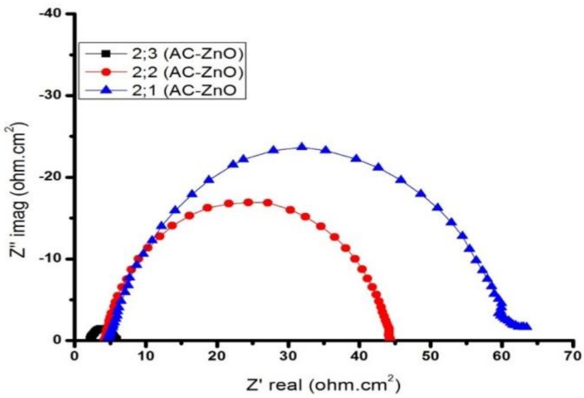

Figure 6. Impedance plots for AC-ZnO composites at compositions of 2:3, 2:2 and 2:1

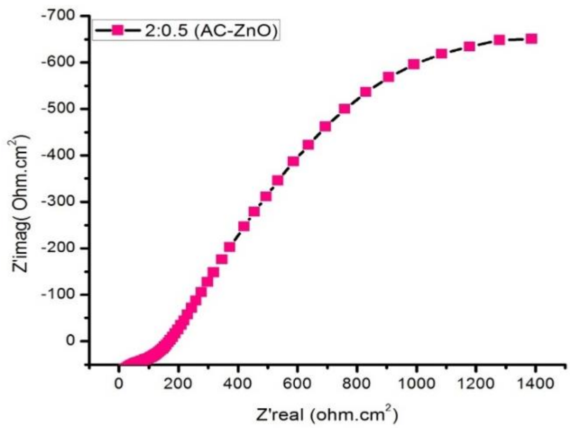

Figure 7. Impedance plots for AC-ZnO composites at 2:0.5 mass ratio.

4. Conclusion

This article describes the use of Setaria verticillata as a bio-reductant in the synthesis of nanostructured ZnO. Through the use of activated carbon composting, bio-synthesised ZnO-NPs functioned as a super capacitor. Using composite electrodes, a super capacitor was created, and its electrochemical characteristics to be investigated by ECI spectroscopy. According to the investigations, super capacitors can be employed as marvellous capacitor active materials since they have superior capacitance.

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References

1. Huanga, N.M., Limb, H.N., Radimanc, S., Khiewd, P.S., Chiud, W.S., Hashime, R., & Chiac, C.H. (2010). Sucrose ester micellar-mediated synthesis of Ag nanoparticles and the antibacterial properties. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 353, 69–76.
2. Nel, A., Xia, T., Madler, L., & Li, N. (2006). Toxic Potential of Materials at the Nanolevel, Science, 311, 622-627.
3. Amornpitoksuk, P., Suwanboon, S., Sangkanu, S., Sukhoom, A., Wudtipan, J., Srijan, K., & Kaewtaro, S. (2011). Synthesis, photocatalytic and antibacterial activities of ZnO particles modified by diblock copolymer. Powder Technology, 212, 432–438.
4. Konenkamp, R., Dloczik, L., Ernst, K., & Olecsh, C. (2002). Nanostructures for solar cells with extremely thin absorbers. Physica E: Low-dimensional systems and Nanostructures, 14, 219–223.
5. Vayssieres, L., Keis, K., Hagfeldt, A., & Lindquist, S.E. (2001). Three dimensional array of highly oriented crystalline ZnO Microtubes. Chemistry of Materials, 13, 4395–4398.
6. Suwanboon, S., Amornpitoksuk, P., Sukolrat, A., & Muensit, N. (2013). Optical and photocatalytic properties of La-doped ZnO nanoparticles prepared via precipitation and mechanical milling method. Ceramics International, 39, 2811-2819.
7. Yilmaz, S., Nisar, J., Atasoy, Y., McGlynn, E., Ahuja. R., & Paralak Bacaksiz, E. (2013). Defect induced room temperature ferromagnetism in B-doped ZnO, Ceramics International, 39, 4609-4617.
8. Taunk, P.B., Das, R., Bisen, D.P., & Raunakkumar, T. (2015). Structural characterization and photoluminescence properties of zinc oxide nano particles synthesized by chemical route method. Journal of Radiation Research and applied sciences, 8, 433-438
9. Kolekar, T.V., Bandgar, S.S., Shirguppikar, S.S., & Ganachari, V.S. (2013). Synthesis and characterization of ZnO nanoparticles for efficient gas sensors. Archives of Applied Science Research, 5, 20–28.
10. Balantrapu, K., & Goia, D. (2009). Silver nanoparticles for printable electronics and biological applications. Journal of Materials Research, 24, 2828–2836.
11. Tripathi, R.M., Saxena, A., Gupta, N., Kapoor, H., & Singh, R.P. (2010). 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, 5, 323–330.
12. Sundrarajan, M., Ambika, S., & Bharathi, K. (2015). Plant-extract mediated synthesis of ZnO nanoparticles using Pongamia pinnata and their activity against pathogenic bacteria, Advanced Powder Technology, 26, 1294-1299.
13. Jeevanandam, J., Chan, Y.S., & Danquah, M.K. (2016). Biosynthesis of metal and metal oxide nanoparticles. ChemBioEng Reviews, 3, 55–67.
14. Shanker, U., Jassal, V., Rani, M., & Kaith, B.S. (2016). Towards green synthesis of nanoparticles: from bio-assisted sources to benign solvents. International Journal of Environmental Analytical Chemistry, 96, 801–835.
15. Wang, G., & Zhang, L., Zhang, J. (2012). A review of electrode materials for electrochemical Super capacitors. Chemical Society Reviews, 41, 797–828.
16. Bose, S., Kuila, T., Mishra, A.K., Rajasekar, R., Kim, N.H., & Lee, J.H. (2012). Carbon based Nanostructured materials and their composites as super-capacitor electrodes. Journal of Material Chemistry, 22, 767-784
17. Wang. J., Gao, Z., Li, Z., Wang, B., Yan, Y., Liu, Q., Mann, T., Zhang, M., & Jiang, Z. (2011). Green synthesis of graphene nanosheets/ ZnO composites and electrochemical properties. Journal of Solid State Chemistry, 184, 1421–1427.
18. Baker, J. (2008). New technology and possible advances in energy storage, Energy Policy, 36,

4368–4373.

19. Selvakumar, M., KrishnaBhat, D., Manish Aggarwal, A., Prahladh Iyer, S., & Sravani, G. (2010). Nano ZnO-activated carbon composite electrodes for super capacitors, Physica B, 405, 2286-2289.
20. Kanagamani, K., Muthukrishnan, P., Saravanakumar, K., Shankar, K., & Kathiresan, A. (2019). Photocatalytic degradation of environmental perilous gentian violet dye using leucaena-mediated zinc oxide nanoparticle and its anticancer activity, Rare metals, 38, 277-286.
21. Bhuyan, T., Mishra, K., Khanuja, M., Prasad, R., & Varma, A. (2015). Biosynthesis of zinc oxide nanoparticles from Azadirachta indica for antibacterial and photocatalytic applications. Materials Science in Semiconductor Processing, 32, 55-61.
22. Sangeethaa, G., Rajeshwari, S., & Venckatesh, R. (2011). Green synthesis of zinc oxide nanoparticles by aloe barbadensis miller leaf extract Structure and optical properties. Materials Research Bulletin, 46, 2560-2566.
23. Abdul Salam, H., Sivaraj, R., & Venckatesh, R. (2014). Green synthesis and characterization of zinc oxide nanoparticles from Ocimumbasilicum L. var. purpurascens Benth.-Lamiaceae leaf extract. Materials Letters, 131, 16-18.
24. Azizia, S., Ahmada, M.B., Namvarb, F., & Mohama, R. (2014). Green biosynthesis and Characterization of zinc oxide nanoparticles using brown marine macroalga Sargassum muticum aqueous extract. Materials Letters, 116, 275-277.
25. Vanathi, P., Rajiv, P., Narendhran, S., Rajeshwari, S., Pattanathu, K.S.M., & Venckatesh, R. (2014). Biosynthesis and characterization of phytomediated zinc oxide nanoparticles:-A green chemistry approach. Materials Letters, 134, 13-15.
26. Li, Z., Liu, P., Yun, G., Shi, K., Lv, X., Li, K., Xing, J., Yang, B. (2014). 3D(Three-dimensional) sandwich structured of ZnO(zinc oxide) /rGO (reduced grapheme oxide) /ZnO for high Performance super capacitors, Energy, 69, 266–271.
27. Hsieh, C.T., Lin, J.S., Chen, Y.F., Lin, C.Y., & Li, W.Y. (2014). Graphene sheets anchored with ZnO nanocrystals as electrode materials for electrochemical capacitors, Materials Chemistry and Physics, 143, 853–859.
28. Zhang, Y., Li, H., Pan, L., Lu, T., & Sun, Z. (2009). Capacitive behaviour of grapheme ZnO composite film for supercapacitors. Journal of Electroanalytical Chemistry, 634, 68–71.