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 Na2SO4 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/cm² 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.

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, etc1–3. 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 bioapplications4–5. Among the various semiconductor nanoparticles, ZnO has received considerable attention because of its unique property of having high excitation binding energy of 60 meV6 and band gap of 3.3 eV7. ZnO-NPs are being synthesised through various physical and chemical methods which includes wet chemical route8, vapour phase process9, hydrothermal10, precipitation11 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 effortless-ness, 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 availablebioresource12–14.
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\textsuperscript{15,16}. Supercapacitors are also known as electrochemical capacitors which find wide applications because of high power density, natural invitingness, long life time and long shelf life\textsuperscript{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 capacitor applications\textsuperscript{19}. In this work, bioinspired ZnO-NPswas synthesized utilizing \textit{Setaria verticillata} 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 \textit{Setaria verticillata} Leaf Extract (SVLE)

\textit{Setaria verticillata} leaves were gathered and utilized for the preparation of aqueous leaf extract of \textit{Setaria verticillata}. 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\textsubscript{3})\textsubscript{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 \textit{Setaria} mediated ZnO-NPs is shown in Figure 1.

2.3 Preparation of \textit{Setaria verticillata} Activated Carbon (SVAC)

\textit{Setaria verticillata} leaves were first washed a few times with demineralized water to expel residue, soil and suspended impurities. The material is ground by using pestle and mortar to turn it into fine particles. About 100g of powdered fine materials was blended with 0.05 L of conc. H\textsubscript{2}SO\textsubscript{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, polyvinylidene 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 performed 0.01 L of 100mM Na\textsubscript{2}SO\textsubscript{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\textsubscript{2}SO\textsubscript{4} at perturbation amplitude of 0.01 V within a frequency range of 0.0001 mHz to 100 mHz.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{Schematic synthetic route of Zinc oxide nanoparticles.}
\end{figure}
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.](image)

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. This is in agreement with the reported work on the eco-friendly synthesis of ZnO-NPs (absorption peak at 374 nm) utilizing various herb extracts, 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 alkenes and C-O stretching, C=O 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 absorption peaks at 1164 cm⁻¹ and 1322 cm⁻¹ are indicative of C=N stretching of amide bonds. In addition, C=O-C stretching vibrations coincide 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 recorded distinctive peak at 490 cm⁻¹ can be ascribed to the [Zn-O] bond of metal oxygen.

![Figure 3.](image)

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 Setaria verticillata 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.

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, 101, 102, 110, 112, 201 and 202 planes respectively. The got outcomes were in appropriate agreement with JCPDS file No. 036-1451 confirming the hexagonal wurtzite structure. The clear severe peak bought suggests the excessive purity and crystalline nature of the synthesised ZnO-NPs. No different diffraction 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.

3.2 Electrochemical Properties of AC-ZnO Composite and Supercapacitors

AC-ZnO nanocomposite 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 Nyquist plots for the AC-ZnO nanocomposite 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-ZnO nanocomposite can be attributed to the electro active property of ZnO supported on activated carbon provides a three-dimensional conducting system which gives active sites for the formation of electrical double layer and pseudo capacitance from the ZnO provides a higher specific capacitance.

Table 1. Electrochemical Impedance parameters for AC-ZnO electrode in 0.1 M Na$_2$SO$_4$.

| 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                  |


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.

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