

Nanoarchitectonics of Zanthoxylum armatum DC. Seed Derived Zinc Chloride Activated Carbon as Negatrode Material for Supercapacitor Applications

Deval Prasad Bhattarai

Tribhuvan University Institute of Science and Technology

Khem Raj Shrestha

Tribhuvan University Institute of Engineering Pulchowk Campus: Tribhuvan University Institute of Engineering

Puspa Lal Homagai

Tribhuvan University Institute of Science and Technology

Timila Shrestha

Tribhuvan University Institute of Science and Technology

Pawan Kumar Mishra

Tribhuvan University Institute of Science and Technology

Hari Bhakta Oli

Tribhuvan University Institute of Science and Technology

Ganesh Prasad Awasthi

Tribhuvan University Institute of Science and Technology

Changho Yu

Tribhuvan University Institute of Science and Technology

Ram Lal (Swagat) Shrestha

ram.shrestha@ac.tu.edu.np

Tribhuvan University - Amrit Campus <https://orcid.org/0000-0002-7939-2830>

Research Article

Keywords: Zanthoxylum armatum, ZnCl₂ activation, Nanoarchitectonics, Activated Carbon Negatrode, Supercapacitor

Posted Date: February 2nd, 2024

DOI: <https://doi.org/10.21203/rs.3.rs-3894119/v1>

Abstract

The storage of green and renewable forms of energy from clean sources has gained considerable attention in the academic as well as industrial arena in the context of ongoing terrible global climatic change. Commonly used carbon nanomaterials are inadequate to address the demand for high-performance energy storage devices due to their high cost, processing difficulties and chances of toxicity. Consequently, facile bio-mass-derived activated carbon is getting more attention due to its high carbon content, more abundant in nature and easiness of processing with minimum toxicity. Here, in this study, we introduced a simple, sustainable approach for the synthesis of ZnCl_2 activated hierarchical 3D network mesoporous/microporous *Zanthoxylum armatum* DC. carbon materials from its precarbonized seed powder at 600, 800 and 1000 °C, respectively. Physicochemical characterization of as-prepared materials was assessed by well-known standard techniques, and energy storage ability was studied in a three-electrode configuration. The electrochemical performance of different sample of zinc chloride activated carbon (ZAC-1000, ZAC-800 and ZAC-600) were compared. ZAC-1000 electrode exhibited the best gravimetric capacitance of 133 F g^{-1} in 1 A g^{-1} with 97.9 % cyclic stability at 10,000 cycles and ~50% rate capability. Based on the findings, highly efficient negative electrode (Negatrod) materials for supercapacitor applications synthesized from the bio-waste seed of *Zanthoxylum armatum* DC. could be useful for commercial applications.

1. Introduction

Extreme use of fossil fuels leads to resource exhaustion, high material cost and detrimental effects on health and environment. Transition to cleaner, sustainable and renewable energy sources from the present condition is indeed a critical global effort aimed at addressing environmental concerns, mitigating climate change and addressing global energy challenges [1]. In the current scenario, the non-renewable fossil fuel reserves will last soon, and its complete replenishment seems impossible. On the other hand, the gradual elevation of the market price of fossil fuel and its serious environmental and economic impact, needs to be addressed instantly to fulfil the energy demand in the near future. Therefore, it is imperative to look at the alternative energy sources. Additionally, renewable, low-cost, environmentally practicable energy sources like wind, geothermal, solar, hydropower, etc., are possible but they are inconsistent and sporadic for long-term and sustainable use. Therefore, sustainable energy storage devices are strongly desirable [2]. In recent decades, supercapacitors, also called ultracapacitors (SCs), and batteries have been used extensively as energy storage devices. Supercapacitor is more popular than batteries due to its simple operating mechanism, low-cost, high-power density, and quick charging-discharging ability with extended cycling life, proficient stability and wide range of working temperature [3]. Theoretically, SCs are categorized into two main classes based on the energy storage mechanism. Supercapacitor which stores energy by electrostatic accumulation of charge/electron absorption and desorption falls into the category of electric double-layer capacitor (EDLC) where carbon-based materials like activated carbon (AC), carbon nanotubes (CNT), graphene, etc., serve as the electrode material. The second type of SCs stores the energy by a faradaic process called the

pseudocapacitor and basically, transition metal compounds exhibit this type of redox energy storage mechanism [4]. Generally, pseudocapacitor possesses better capacitance and energy density as compared to EDLC type, but they lack cyclic stability and low retention capability, hence limiting them from commercialization. On the other hand, in the case of EDLC type SC, electrostatic charges arise on the surface of electrode materials or within the double layers and facilitates in energy storage, high power supply with delivering substantial capacitance and proficient energy storage capabilities. The efficiency of EDLC depends upon the structural arrangement and electrochemical properties of electrode materials [5, 6].

In the field of supercapacitor, design of bio-mass derived activated carbon (AC) based electrode is in the forefront because of its cheap price, high carbon content with the possibility of self-doped heteroatoms and readily available precursor. AC can be easily prepared from biomass using sustainable sources such as peanut shells, bagasse, rice husks, coconut shells, bamboo, litchi seed, cashew nutshells, and *Zanthoxylum schinifolium* husk, etc. [7–9]. Even though bio-waste derived activated carbon has many merits and is sustainable material for the long run energy storage, it still has some drawbacks like variability in feedstock (bio-source) quality, difficulty in controlling the pore size structure, basically having reduced surface area, probability of containing ash with longer scalability and environmental regulatory problem with authentic certification challenge [10–13].

Electrodes derived from biowaste source for SCs applications can exhibit wide potential window in electrochemical assessment in addition to the solution of waste management. Additionally, it provides a wide range of composite assemblages with new developments and regulation of optimum electrodes according to the merits of the different qualities of activated carbon. The self-doped hetero-elements containing carbon-rich bio-waste are in huge abundance in the verities of the AC derived from the different livestock by controlling the degree of graphitization and defect. Such materials are of immense uses in the field of energy storage due to their significant conductivity. Some substances like walnut shell, pear stone, pistachio shell, and seed of *Zanthoxylum armatum* DC, etc., have hard surface and unique structure of ligno-cellulosic mass. Preparation of activated carbon from such materials can lead to the generation of unique pore-structure in the activated carbon. Therefore, such types of materials could be executed for the preparation of electrode materials with chemical stability, high carbon content and porous large surface structure [14–16].

In this work, porous activated carbon is prepared from the seeds of *Zanthoxylum armatum* DC. Normally, the outer part of the *Zanthoxylum* is consumed for culinary and medicinal purposes due to anti-inflammatory as well as anti-oxidant properties. On the other hand, the seed part of *Zanthoxylum armatum* DC is commonly discarded and considered as waste. Here, this part of materials was taken and executed for the preparation of activated carbon by facile and scalable heat treatment carbonization process. A thorough literature review showed that no work had been reported on supercapacitor electrode application from activated carbon derived from the seeds part of *Zanthoxylum armatum*. The precarbonized carbon was chemically activated using zinc chloride, followed by carbonization under different temperatures in a nitrogen atmosphere to design nanoporous carbon materials, a paradigm of

carbon nanoarchitectonics. Nanoarchitectonics can be of great use in the creation of nanoscale structure of particular interest. Here, physicochemical and electrochemical characterization of the material revealed the preparation of nanoporous activated carbon from the waste biomass. As-prepared activated carbon exhibited 133 F g^{-1} capacitance at a current density of 1 A g^{-1} with good cycling stability. Based on the finding, it is revealed that the *Zanthoxylum armatum* DC seeds powder has great potential as a negative electrode (negatrode) of supercapacitor device due to the large surface area and uniform distribution of meso/micropores structure and better cyclic stability.

2. Experimental section

2.1 Reagents

Zinc chloride (ZnCl_2 , Mol. Wt. 136.30 g/mol, purity $\geq 85\%$, Merck Life Science), potassium hydroxide (KOH, Mol. Wt. 56.11, NIKE), hydrochloric acid (HCl, Mol. Wt. 36.46, Fischer Scientific, purity 35–37%), sodium hydroxide (NaOH, Mol. Wt. 40.00, NIKE, purity $\geq 97\%$), polyvinylidene fluoride (PVDF), N-methylpyrrolidone (NMP), Ni foam, isopropyl alcohol, ethanol were used in this work. All the chemicals were of analytical grades and were used as-received without further purification.

2.2 Synthesis

2.2.1 Collection and pulverization of the sample

The raw material, *Zanthoxylum armatum* DC, was collected from the Palung, Makawanpur district of Nepal. The seed portion, the waste part of *Zanthoxylum armatum* DC, was extracted and oven-dried at 80°C for a whole night. The sample was then pulverized into the raw powder form using herbal medicine disintegrator (FW177). The sample was dried at 100°C in the general oven for 3h.

2.2.2 Synthesis of porous activated carbon

The dried sample was then impregnated with chemical activator ZnCl_2 by fraternization, in the ratio of 1:1 followed by grinding properly for 3 h in the agate mortar pestle. In detail, 10 g of raw powder sample was mixed with 10 g of zinc chloride and ground appropriately to make a uniform fine powder using agate mortar pestle. It was then, introduced into the muffle furnace and precarbonized for 3 h at 400°C . Afterwards, the sample was divided into three parts to make three different temperature-dependent zinc chloride activated carbon (ZAC) *i.e.*, 600, 800 and 1000°C . These samples were correspondingly named as, ZAC-600, ZAC-800 and ZAC-1000. The carbonization process was carried out under the same condition in a tube furnace (KJ-T1200 Tube Furnace, Zhengzhou Kejia Furnace Co., Ltd, China) under an inert atmosphere (N_2 gas) for 3 h with a ramping rate 5°C min^{-1} with a nitrogen flow at 120 cc min^{-1} but at different temperature. Then, the sample was ground in an agate mortar pestle to make it more homogeneous. Later on, each sample was transferred into a beaker of 250 mL capacity and mixed with 10 mL of 1 M HCl slowly with continuous stirring followed by adding another 150 mL DW water. The mixture was stirred magnetically for 30 min. Then it was left for 1 hour for decantation. After that, the

supernatant liquid was removed carefully, and the sediment sample was washed with distilled water till it attained almost neutral pH value. Finally, the sample was vacuum dried at 80°C for 6 h. As-obtained ACs were again ground in a mortar pestle and stored in a desiccator for further study and characterization.

2.3 Characterization

2.3.1 Material characterization

The room temperature powder x-ray diffraction (PXRD) patterns of the as-prepared samples were recorded using a Rigaku Diffractometer under the operation of 40 kV and 40 mA with CuK_α source (wavelength $\lambda = 1.54059 \text{ \AA}$) at a rate of $2.5^\circ \text{ min}^{-1}$ in the range of $5-80^\circ$. Raman spectra of the samples were recorded on a Renishaw in Via Raman Microscope with a 532 nm green light laser at 0.01 mW power by putting the samples on a glass slab. The presence of a surface functional group of activated carbon was ensured by recording the Fourier transform Infra-red (FTIR) spectrometer (IR Prestige 21-FTIR Spectrometer, SIMADZU, Sendai, Japan) by attenuated total reflection (ATR) mode in the range of 4000 cm^{-1} to 400 cm^{-1} at 25°C . A field emission scanning electron microscope (FESEM, Hitachi, Tokyo, Japan) was used to study the surface morphology of the activated carbon. FESEM equipped with Energy dispersive x-ray (EDX) was used to quantify the composition and distribution of elements in the sample. Surface areas and porosity of activated carbon prepared at different temperatures were investigated by the Brunauer-Emmett-Teller (BET) surface area measurement and Barrett-Joyner-Halenda (BJH) method using Quantachrome instrument (Quadrasorb SI Automated surface area and pore size analyzer, Florida) in the surface chemistry laboratory in JNCASR, Bengaluru, India. The surface area of ZAC was measured by the nitrogen gas adsorption-desorption method in a relative pressure range of 0 to 1 Pascal at 77 K temperature. Following BET equation was used for the determination of the surface area of the material.

The BET equation is
$$\frac{1}{V[(\frac{P_0}{P})-1]} = \frac{(C-1)}{V_m C} (\frac{P}{P_0}) + \frac{1}{V_m C}$$

Where V is the volume of adsorbed gas, V_m is the volume (at STP) of nitrogen gas adsorbed onto the monolayer surface, P_0 is the saturated pressure of adsorbate gas, P is the partial vapor pressure of adsorbate gas in equilibrium with surface at 77.3 K, C is constant which is related to the enthalpy of adsorbate gas on the sample, P/P_0 is the relative pressure.

2.3.2 Electrochemical characterization

Cyclic voltammetry (CV), Galvanostatic charge-discharge (GCD), and electrochemical impedance spectroscopy (EIS) of the sample were measured using Electrochemical Zive SP₂ instrument.

Electrochemical measurements were carried out in a three-electrode system with active material deposited onto nickel foam. Silver/Silver Chloride (3 M KCl) electrode was used as a reference electrode in 3 M KOH solution. A platinum electrode was used as the counter electrode.

First of all, 10% by wt. of PVDF was dissolved in NMP solvent. 80% active sample and 10% carbon black were ground in a mortar and then mixed with previously prepared NMP solution. After that, the homogeneous slurry was drop-casted onto the previously washed nickel foam (1 × 1 cm) and dried at 60 °C for 12 h. The nickel foam had an active mass of 4 mg/cm² and was used as a working electrode for electrochemical tests. The CV and GCD measurements were recorded within the potential window of -1 to 0 V under different scan rates. In addition, the electrochemical impedance spectra were measured on a Nyquist plot in the frequency range of 0.01 Hz to 100 kHz. The capacitances (C) of the electrode material were calculated from the Galvanic-charged discharged curve using the following relation.

$$C = \frac{I \times \Delta t}{A \times \Delta v}$$

Herein, I is charge-discharge current, Δt is discharge time (in seconds), A is the area of the electrode, and Δv is the difference in the potential window (in volts).

3. Results and Discussion

An efficient carbonization process was carried out for the synthesis of activated carbon from the seeds of *Zanthoxylum armatum* DC. Activation process prompts the porosity of materials with multichannel networks resulting into high surface area [17]. Figure 1 displays the schematic diagram for the synthesis process of activated carbon. Basically, activation is carried out by physical and chemical processes. Physical activation involves heating of carbon-rich material to high temperatures (600–1000 °C) in nitrogen atmosphere [18]. This dispels the volatile matter and leaves behind a porous 3D carbon structure. On the other hand, uses of chemical activating agent such as ZnCl₂ generates a porous 3D carbon structure by sacrificing the activating agent through etching away some carbon in the form of CO₂. Here in our study, we carried out both physical and chemical activation process simultaneously at different temperature ranging from 600–1000 °C. This will add more benefits of producing high-quality activated carbon. It willingly advances fundamental properties like increased surface area, improved adsorption capacity, increased selectivity with enhanced activation site for the ion/electron exchange [19]. The pulverized sample obtained from the bio-source *Zanthoxylum armatum* DC seed was pre-heated to 400 °C to remove the moisture and some of the low boiling volatile organic substances. The sample was then mixed with the activating agent ZnCl₂ in a definite proportion (1:1) and subjected to temperature-dependent heat treatment process. The samples were calcined at three different temperatures viz. 600 °C, 800 °C and 1000 °C under the Nitrogen atmosphere, and correspondingly, the samples were named ZnCl₂ activated carbon (ZAC) as ZAC-600, ZAC-800, ZAC-1000, respectively. Moreover, when the pulverized mass of *Zanthoxylum armatum* DC seed is mixed with activator ZnCl₂, impregnation takes place, where ZnCl₂ breaches the porous carbon, leading to the splitting into respective Zn²⁺ and Cl⁻ ions. The Zn²⁺ possibly reacts with the bio-molecules present (particularly with proteins and enzymes) in the sample through the coordination bonds. This may result into the denaturation of proteins and enzymes by disrupting the structure. Due to this disruption of complex structures formed with Zinc ions and bio-molecules, further degradation will be prompted. Moreover, the carbon also makes a

complex with these ionized activators resulting into the carbon surface functionalization by Lewis acid-base interaction. On the other hand, Zinc chloride, itself a dehydrating agent, removes the moisture and creates an environment for leading the porosity procession and also lead to the formation of the stable complex with carbon and zinc/oxygen/chloride compound ($\text{ZnCl}_2 + 2 \text{H}_2\text{O} \rightarrow \text{Zn}_2\text{OCl}_2 \cdot 2\text{H}_2\text{O}$). As the temperature increases (up to $\sim 1000^\circ\text{C}$) in an inert nitrogen atmosphere, decomposition of the Zinc-carbon complex as well as zinc/oxygen/chlorine compounds ($\text{Zn}_2\text{OCl}_2 \cdot 2\text{H}_2\text{O} \rightarrow \text{ZnO} + \text{ZnCl}_2 + \text{H}_2$) takes place, leading to the evolution of the ZnO, ZnCl_2 and H_2 in the form of vapor resulting into the development of voids or pores. Additionally, Zinc (II) oxide formed during *in situ* reaction also gets reduced to zinc vapor ($2 \text{ZnO} + \text{C} \rightarrow 2 \text{Zn} + \text{CO}_2$) and escapes out making a route for formation of various sizes of void in the samples. According to the demand, the 3D carbon structure expands, causing a large surface area. The size of the pores varies with the materials and condition of the carbonization time, which finally leads to the formation of mesoporous and microporous sizes. Additionally, ZnCl_2 also acts as a coagulating agent. It flocculates the unwanted suspended solids and leads to settling down, which helps to separate solid from liquid phases, simplifying successive treatment levels. Here, the reaction is carried out at $600\text{--}1000^\circ\text{C}$ in a tube furnace under a nitrogen atmosphere, Zinc and its derivate are removed from the activated carbon because of the low boiling point of the zinc (907°C) and ZnCl_2 (723°C). Hence, there is the least chances of attachment of Zinc and its complex remaining in the final sample. Therefore, ZnCl_2 acts as the sacrificing agent for activating the bio-source materials into the activated carbon. These samples are further characterized in terms of XRD, EDX and XPS analysis [20–22].

The phase purity and crystallinity of the bio-waste derived ZnCl_2 activated carbon (ZAC) was investigated using powder X-ray diffraction (PXRD) analysis (Fig. 2A). It revealed the phase purity of all precarbonized-400, ZAC-600, ZAC-800 and ZAC-1000 samples. Furthermore, it shows a prominent broad diffraction peak at $2\theta = \sim 23.58^\circ$, (d – spacing $\sim 0.37 \text{ nm}$) corresponding to the (002) plane of carbon materials and another broad diffraction peak at $2\theta = \sim 43.8^\circ$ (d – spacing $\sim 0.21 \text{ nm}$) corresponding to the (001) plane of graphitic nature of carbon [5, 23]. In this study, we have not noticed any diffraction peaks due to activator ZnCl_2 at any temperature, indicating pure carbon formation. It shows that ZnCl_2 only activates the carbon materials for the rapid ions/electron transport without having any carbon zinc complex in any types of carbon materials [24]. This is supported by the EDX mapping results and XPS analysis as shown in the S1 and Fig. 4, respectively. In order to identify the unknown materials, present in the as-prepared sample, FTIR was performed and shown in Fig. 2B. No prominent peaks are observed in the sample, which ratifies that the activated carbon obtained from the seed of *Zanthoxylum armatum* DC contains only carbon structure [25]. Theoretically, the surface area and porosity of the materials are the major parameter to evaluate the materials for the supercapacitor applications. All the carbonized samples of ZAC-600, ZAC-800 and ZAC-1000 were analyzed by BET analysis at nitrogen adsorption-desorption at -196°C . BET plot (Fig. 2C) shows that ZAC-1000 has the highest surface area (about $2180 \text{ m}^2 \text{ g}^{-1}$) compared to other samples (specific surface area of ZAC-600 and ZAC-800 are $956 \text{ m}^2 \text{ g}^{-1}$, and $1171 \text{ m}^2 \text{ g}^{-1}$, respectively) (Fig. S2A, S3A, respectively). This could be associated with graphitic carbonization. The

nature of adsorption-desorption isotherm of ZAC-1000 fully agrees with type II isotherm with a hysteresis. The larger surface area of ZAC-1000 is due to the various forms of voids (pores) present in the sample resulted due to the removal of zinc/carbon/oxygen compounds forming a route of escaping. The exponential increase in adsorption value at low relative pressures ($P/P_0 < 0.2$) is associated with the presence of micropore. However, the presence of a hysteresis loop from a relative pressure (P/P_0 at 0.5 to 1) indicates as the presence of mesopores [2, 7]. Furthermore, the pore size distribution was estimated by applying the BJH method, and it was found to be between 4 to 8 nm in the case of ZAC-1000. The improved specific surface area, along with its mesoporous nature makes the ZAC-1000 an ideal material for Supercapacitors application. Besides these, the counter samples also possess the mesoporosity with pore size ranges from 5 to 10 nm, shown in fig. S2B, S3B, in supporting file.

The 3D morphology of ZAC samples was examined by FESEM analysis at different magnifications. Figure 3 displayed the FESEM image of the ZAC prepared under different carbonization temperatures. FESEM images of ZAC revealed a massive, porous arrangement with a range of porosity, in size and shape. These pores are interconnected, forming a complex giant network of channels, which can trap and allow the electrons/ions for the freeway passage. Besides this, other types of functional groups present in activated carbon with oxygen make it more reliable for further enhancement in its adsorption capacity of the charge/electron/ions. Among the ZAC materials, ZAC-1000 has a fine network as observed in low as well as high magnification due to the evaporation of all the impurities. On the other hand, the ZAC-800 and ZAC-600 also possess similar types of morphology but have rough surfaces, less porosity and larger particles network.

The metallic vibrations and the presence of carbon and its nature in bio-waste derived ZnCl_2 activated carbon were further characterized by Raman spectroscopic analysis in the wavenumber range from 500 to 2500 cm^{-1} ($\lambda = 514\text{ nm}$). The results are displayed in Fig. 4A. The Raman spectra of all these four types of bio-waste derived ZnCl_2 activated carbon exhibited the broad D – band (defect – induced mode) at $1320\text{--}1350\text{ cm}^{-1}$ and the G band (graphite E_{2g} mode) at $1570\text{--}1600\text{ cm}^{-1}$ [26]. The I_D/I_G values of precarbonized-400, ZAC-600, ZAC-800 and ZAC-1000 samples were found to be 0.86, 0.93, 1.01 and 0.99, respectively, which confirms the presence of a graphitic nature of activated carbon caused by temperature-dependent carbonization. Moreover, there is no prominent 2D band as, the samples were derived from the bio-source and have a normally lower degree of graphitization [2, 6, 7].

To confirm the chemical composition of the as-prepared activated carbon, X-ray photoelectron spectroscopy (XPS) was performed (Fig. 4). The survey spectrum (Fig. 4B.) reveals the peaks of carbon and trace amount of oxygen. The deconvoluted spectrum of the C1s displayed the peaks at 284.1 eV, 285.4 eV and 286.7 eV corresponding to the $\text{C}=\text{C}$ (sp^2), $\text{C}-\text{C}$ (sp^3) and $\text{C}-\text{O}-\text{C}/\text{C}-\text{OH}$ groups, respectively. Additionally, the deconvoluted spectrum of O1s is displayed in Fig. 4D. It has three major peaks at 531.6 eV, 532.7 eV and 535.1 eV, which corresponds to the $-\text{C}=\text{O}$, $-\text{C}-\text{O}-\text{C}$, and $-\text{COOH}$ groups of the oxygen. The presence of oxygen could be associated with the oxygen functionalized carbon or adsorbed moisture [27].

4. Electrochemical Study

To enumerate the potential practical applicability of the electrode materials for supercapacitors, the electrochemical performance of ZAC samples was measured in 6 M KOH solution in three-electrode configurations. Cyclic voltammetry (CV) curves of all three samples showed a nearly rectangular shape. The CV was measured under the potential window from -1.0 to 0.0 V. Due to appropriate carbonization, the sample ZAC-1000 has the perfect rectangular shape of EDLC type, while ZAC-800 and ZAC-600 convey some sort of distortion from the ideal EDLC type. Figure 5A shows the comparative CV plot of ZAC under the same scan rate (10 mVs^{-1}). Among them ZAC-1000 has the largest CV area than the ZAC-800 and ZAC-600 activated carbon samples. It indicates the improved capacitance (C_{sp}) compared to other activated carbon. This is due to optimization and high-temperature carbonization, which can create enough pores on its surface and provide a large surface area for the electrode/electrolyte ions adsorption. Figure 5B shows the CV plots of ZAC-1000 in different scan rates $10\text{--}100 \text{ mV s}^{-1}$. It has the perfect rectangular EDLC-type, and the area of the CV plot increases linearly with increasing scan rate, which gives better reversibility of the samples. Theoretically, as the scan rate increases, double-layer charging and discharging occurs, which increases the capacitive current and thinning of the diffusion layer of the solution near the electrode surface (The thickness of the diffusion layer is inversely proportional to the square root of the scan rate) [1, 2, 23]. Hence, as the scan rate increases, the diffusion layer thickness decreases, which allows more reactant species to reach the electrode surface reaction. Similarly, in ZAC-800 and ZAC-600 samples, the area of the CV curve increases with increases in scan rate, which are shown in S4A and S5B, respectively.

Furthermore, to compute the performance value of ZAC samples in specific capacitance (C_{sp}) Galvanostatic charge-discharge (GCD) was performed in 6 M KOH under the potential window of -1.0 to 0 V at various current density ranging from $1\text{--}15 \text{ A g}^{-1}$. Figure 5C shows the GCD curve of the ZAC-1000 sample while fig.S4B and S5B show the GCD plot of the ZAC-800 and ZAC-600, which displayed the perfect linear charging-discharging curves with respect to time. It shows the perfect EDLC-type plot without any peaks due to non-redox adsorption/desorption of electrons/ions inside the delicate, easy penetration of porous activated carbon network from the electrode/electrolyte interface [28]. As compared to the ZAC-800 and ZAC-600, ZAC-1000 shows more symmetry in the charging-discharging phenomenon because of better carbon network of $\text{-C}=\text{C-}$ providing a more electroactive site for electron accumulation, so it possesses the improved capacitance than the other samples shown in Fig. 5D. The calculated gravimetric specific capacitance for ZAC-1000 sample are, 133, 109, 92, 86, 81, 71 and 61 F g^{-1} at current densities of 1, 2, 3, 4, 5, 10 and 15 A g^{-1} , respectively. While, the samples ZAC-800 and ZAC-600 displayed the specific capacitance 107, 88, 72, 59, 48, 34, 27 F g^{-1} and 85, 70, 61, 48, 37, 29, 21 F g^{-1} under the respective current density of 1, 2, 3, 4, 5, 10, and 15 A g^{-1} , respectively. Here, the decreasing trends of specific capacitance in higher current density are more common in three-electrode system. This is due to the internal resistance of active materials present in working electrode materials, corresponds to their higher IR drop at higher current density. The final sample ZAC-1000, retains its initial rate capability $\sim 50\%$, while other samples have rate capacity retention $\sim 41\%$ and $\sim 40\%$ for respective samples ZAC-800

and ZAC-600. Basically, the low retention rate capability is due to the inadequate electrode conductivity and electrode/electrolyte insufficient interaction; however, ZAC-1000 is quite better than the counter sample due to the large surface area with a larger activation site for the accumulation of the higher electron density under same area [29]. Moreover, due to the dependent high-temperature carbonization process, it leads to more graphitization with a large amount of sp^2 carbon network and has more consistency on porosity (mesoporosity/microporosity) [30].

To know the charge transfer kinetics for the ZAC samples, electrochemical impedance spectroscopy (EIS) was studied. Theoretically EIS plot consists of three major portion, high frequency charge transfer kinetics (R_{ct}), middle Warburg impedance and low frequency inclined capacitive nature, and the schematic figure is displayed in S6 [31]. The Nyquist plot of all different ZAC samples are shown in Fig. 5E in the range of 100 kHz to 0.01 Hz with an applied potential 0.5 mV. Among the ZAC samples, ZAC-1000 owed the lower R_{ct} value (5.48 Ω) with parallel inclined lower frequency region to the imaginary axis which suggest the more diffusion of electrolyte ions into the electrode, while in case of the other samples ZAC-800 and ZAC-600 has the larger high frequency region and the lower frequency regions are also not parallel (less inclined) and deviates from the imaginary axis, hence lower ionic mobility and hence lower capacitive values. The R_{ct} value for the ZAC-800 and ZAC-600 has 17.3 Ω and 116.3 Ω respectively, which is extremely higher than the R_{ct} values of the ZAC-1000.

For the real practice and commercial viability of the electrode materials, cyclic stability is the prime important parameter. Principally, the higher the stability of the materials during repeated cycles of GCD in higher current density, the more appropriate will be the electrode materials for real application. Here, the final sample ZAC-1000 was subjected to cyclic stability at 15 A g^{-1} for 10,000 cycles and found to be 97.9% cycle life. The good cyclic stability of the materials are due to the following reasons (i) ion tunneling effect during charging and discharging (ii) higher surface area of the ZAC-1000 provides more activated sites for the electron/ion adsorption and desorption (iii) high temperature carbonization of the biomass-derived complex structure leads to more uniform pores in activation process (iv) presence of heteroatoms like oxygen which provides surface wettability and better electrochemical activity with durable charge-discharge cycle [1, 3, 28]. During stability test some cycle $\sim$ 1600–2000 and $\sim$ 3500–5000 has the variability due to the structural variation and has some lacking on carbonization. The EIS was measured before and after the cyclic stability shown in fig S7. It displayed almost identical types of EIS plots. There is no significant change in charge transfer kinetics before and after the 10,000 cycles. Finally, it is worth revealing that biomass-derived activated carbon has different merits in conducting materials like better specific capacitance cycle life and an enormously larger specific surface area. Therefore, the novel activated carbon ZAC-1000 can be considered a suitable material as an anode material in supercapacitor applications in device fabrication.

5. Conclusions

In summary, we have successfully prepared the 3D network ZnCl_2 activated mesoporous/microporous carbon materials (ZAC) from the seed of *Zanthoxylum armatum* DC by facile carbonization method with zinc chloride activation in 1:1 ratio by weight. Different physicochemical characterization revealed the formation of highly porous activated carbonaceous materials with profound porosity. Activated carbon prepared by chemical activation at 1000°C exhibited the surface area of $2180\text{ m}^2\text{ g}^{-1}$. The electrochemical performance was compared, and found that ZAC-1000 has a better capacitance of 133 F g^{-1} at 1 A g^{-1} with good cycle life (97.9% in 10,000 cycle) and better rate capability ($\sim 50\%$) due to the smoother surface with uniform meso/microporosity formation. Based on the finding, it is revealed that this material can potentially act as negatrode or anode material in the fabrication of the device system supercapacitor.

Declarations

Conflicts of interest

All authors declare that, we have no known competing interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This research was supported by University Grant Commission, Nepal (Faculty Research Grant: FRG 77/78-S&T-3. Authors are grateful to the Center for University-Wide Research Facilities (CURF) at Jeonbuk National University for the instrumental assistance.

References

1. K. R. Shrestha, S. Kandula, G. Rajeshkhanna, M. Srivastava, N. H. Kim, and J. H. Lee, An advanced sandwich-type architecture of $\text{MnCo}_2\text{O}_4@\text{N-C}@\text{MnO}_2$ as an efficient electrode material for a high-energy density hybrid asymmetric solid-state supercapacitor, *J. Mater. Chem. A*, 6, (2018), 24509. <https://doi.org/10.1039/C8TA08976K>
2. G. Dhakal, D. Mohapatra, Y.-Il Kim, J. Lee, W. K. Kim, J.-J. Shim, High-performance supercapacitors fabricated with activated carbon derived from lotus calyx biowaste, *Renewable Energy*, 189 (2022) 587-600. <https://doi.org/10.1016/j.renene.2022.01.105>
3. J. Sun, B. Luo, H. Li, A Review on the Conventional Capacitors, Supercapacitors, and Emerging Hybrid Ion Capacitors: Past, Present, and Future, *Adv. Energy Sustainability Res.* 3, (2022), 2100191. <https://doi.org/10.1002/aesr.202100191>
4. S. Najib, E. Erdem, Current progress achieved in novel materials for supercapacitor electrodes: mini review, *Nanoscale Adv.*, 1, (2019), 2817. <https://doi.org/10.1039/C9NA00345B>

5. K. R. Shrestha, S. Kandula, N. H. Kim, J. H. Lee, Core cation tuned $\text{MxCo}_3\text{-xS}_4\text{@NiMoS}_4$ [M = Ni, Mn, Zn] core-shell nanomaterials as advanced all solid-state asymmetric supercapacitor electrodes, *J. Chem. Eng.*, 405 (2021) 127046. <https://doi.org/10.1016/j.cej.2020.127046>
6. B. Pant, G. P. Ojha, J. Acharya, H. R. Pant, M. Park, Lokta paper-derived free-standing carbon as a binder-free electrode material for high-performance supercapacitors, *Sustainable Materials and Technologies* 33 (2022) e00450. <https://doi.org/10.1016/j.susmat.2022.e00450>
7. G. Dhakal, D. R. Kumar, S. Sahoo, J.-J. Shim, Litchi seed biowaste-derived activated carbon supporting matrix for efficient symmetric and asymmetric supercapacitors, *Carbon* 208 (2023) 277-289. <https://doi.org/10.1016/j.carbon.2023.03.045>
8. C. Liu, F. Li, L. P. Ma, H. M. Cheng, Advanced Materials for Energy Storage, *Adv. Mater.* 22, (2010), E28-E62. <https://doi.org/10.1002/adma.200903328>
9. S. Sundriyal, V. Shrivastav, H. D. Pham, S. Mishra, A. Deep, D. P. Dubal, Advances in bio-waste derived activated carbon for supercapacitors: Trends, challenges and prospective, *Resources, Conservation & Recycling* 169 (2021) 105548. <https://doi.org/10.1016/j.resconrec.2021.105548>
10. H. Yang, S. Ye, J. Zhou, T. Liang, Biomass-Derived Porous Carbon Materials for Supercapacitor, *Front. Chem.* 7, (2019), 274. <https://doi.org/10.3389/fchem.2019.00274>
11. A. Divyashree, S. A. B. A. Manaf, Yallappa S, Chaitra K, Kathyayini N, G. Hegde, Low cost, high performance supercapacitor electrode using coconut wastes: eco-friendly approach, *J. Energy Chem.*, 25, (2016), 880-887. <https://doi.org/10.1016/j.jechem.2016.08.002>
12. Y. A. Haj, S. Mousavihashemi, D. Robertson, M. Borghei, T. Paakkonen, O. J. Rojas, E. Kontturi, T. Kallio, J. Vapaavuori, Biowaste-derived electrode and electrolyte materials for flexible supercapacitors, *J. Chem. Eng.*, 435, (2022), 135058. <https://doi.org/10.1016/j.cej.2022.135058>
13. T. Noszczyk, A. Dyjakon, J. A. Koziel, Kinetic Parameters of Nut Shells Pyrolysis, *Energies* 14, (2021), 682. <https://doi.org/10.3390/en14030682>
14. G. A. Tafete, M. K. Abera, G. Thothadri, Review on nanocellulose-based materials for supercapacitors applications, *J. Energy Storage* 48, (2022), 103938. <https://doi.org/10.1016/j.est.2021.103938>
15. E. Elanthamilan, B. C. Meena, N. Renuka, M. Santhiya, J. George, E.P. Kanimozhi, J. C. Ezhilarasi, J. P. Merlin, Walnut shell derived mesoporous activated carbon for high performance electrical double layer capacitors, *J. Electroanal. Chem.* 901, (2021), 115762. <https://doi.org/10.1016/j.jelechem.2021.115762>
16. Y. Guo, C. Liu, L. X. Yin, X. X. Zhang, Y. Q. Shan, P. G. Duan, Preparation of supercapacitor carbon materials from food waste via low-temperature pyrolysis, *Journal of Analytical and Applied Pyrolysis*, 170, (2023), 105880. <https://doi.org/10.1016/j.jaap.2023.105880>
17. T. Subramaniam, M. A. M. Nainar, N. A. Nordin, A Review on Synthesis and Characterization of Activated Carbon from Natural Fibers for Supercapacitor Application, *Pertanika J. Sci. & Technol.* 30, (2022), 351-376. <https://doi.org/10.47836/pjst.30.1.20>
18. K. Surya, M.S. Michael, Hierarchical porous activated carbon prepared from biowaste of lemon peel for electrochemical double layer capacitors, *Biomass Bioenergy*, 152, (2021), 106175.

<https://doi.org/10.1016/j.biombioe.2021.106175>

19. B. Li, J. Hu, H. Xiong, Y. Xiao, Application and Properties of Microporous Carbons Activated by ZnCl₂: Adsorption Behavior and Activation Mechanism, *ACS Omega*, 5, (2020), 9398–9407.
<https://doi.org/10.1021/acsomega.0c00461>
20. D. Bosch, J. O. Back, D. Gurtner, S. Giberti, A. Hofmann, A. Bockreis, Alternative feedstock for the production of activated carbon with ZnCl₂: Forestry residue biomass and waste wood, *Carbon Resources Conversion*, 5, (2022), 299-309. <https://doi.org/10.1016/j.crcon.2022.09.001>
21. Y. Gao, Q. Yue, B. Gao, A. Li, Insight into activated carbon from different kinds of chemical activating agents: A review, *Sci. Total Environ.*, 746, (2020) 141094.
<https://doi.org/10.1016/j.scitotenv.2020.141094>
22. Y. Wang, Q. Qu, S. Gao, G. Tang, K. Liu, S. He, C. Huang, Biomass derived carbon as binder-free electrode materials for supercapacitors, *Carbon*, 155, (2019), 706-726.
<https://doi.org/10.1016/j.carbon.2019.09.018>
23. G. Shi, C. Liu, G. Wang, X. Chen, L. Li, X. Jiang, P. Zhang, Y. Dong, S. Jia, H. Tian, Y. Liu, Z. Wang, Q. Zhang, H. Zhang, Preparation and electrochemical performance of electrospun biomass-based activated carbon nanofibers, *Ionics*, 25, (2019), 1805-1812. <https://doi.org/10.1007/s11581-018-2675-3>
24. S. Minaei, K. Z. Benis, K. N. McPhedran, J. Soltan, Evaluation of a ZnCl₂-modified biochar derived from activated sludge biomass for adsorption of sulfamethoxazole, *Chem Eng Res Des*, 190, (2023), 407-420. <https://doi.org/10.1016/j.cherd.2022.12.038>
25. A. Y. Elnour, A. A. Alghyamah, H. M. Shaikh, A. M. Poulouse, S. M. Al-Zahrani, A. Anis, M. I. Al-Wabel, Effect of Pyrolysis Temperature on Biochar Microstructural Evolution, Physicochemical Characteristics, and Its Influence on Biochar/Polypropylene Composites, *Appl. Sci.* 9, (2019), 1149.
<https://doi.org/10.3390/app9061149>
26. P. Sharma, D. Singh, M. Minakshi, S. Quadsia, R. Ahuja, Activation-Induced Surface Modulation of Biowaste-Derived Hierarchical Porous Carbon for Supercapacitors, *ChemPlusChem*, 87, (2022), 1-14. <https://doi.org/10.1002/cplu.202200126>
27. Z. Bi, Q. Kong, Y. Cao, G. Sun, F. Su, X. Wei, X. Li, A. Ahmad, L. Xie, C. M. Chen, Biomass-derived porous carbon materials with different dimensions for supercapacitor electrodes: a review, *J. Mater. Chem. A*, 7, (2019), 16028. <https://doi.org/10.1039/C9TA04436A>
28. S. Kandula, K. R. Shrestha, N. H. Kim, J. H. Lee, Fabrication of a 3D Hierarchical Sandwich Co₉S₈/α-MnS@N-C@MoS₂ Nanowire Architectures as Advanced Electrode Material for High Performance Hybrid Supercapacitors, *Small* (2018), 1800291. <https://doi.org/10.1002/smll.201800291>
29. S. Saini, P. Chand, A. Joshi, Biomass derived carbon for supercapacitor applications: Review, *J. Energy Storage*, 39, (2021), 102646. <https://doi.org/10.1016/j.est.2021.102646>
30. G. S. d. Reis, S. H. Larsson, H. P. de Oliveira, M. Thyrel, E. C. Lima, Sustainable Biomass Activated Carbons as Electrodes for Battery and Supercapacitors-A Mini-Review, *Nanomater.*, 10, (2020), 1398.
<https://doi.org/10.3390/nano10071398>

31. B. A. Mei, O. Munteshari, J. Lau, B. Dunn, L. Pilon, Physical Interpretations of Nyquist Plots for EDLC Electrodes and Devices, J. Phys. Chem. C, 122, (2018), 194–206.
<https://doi.org/10.1021/acs.jpcc.7b10582>

Figures

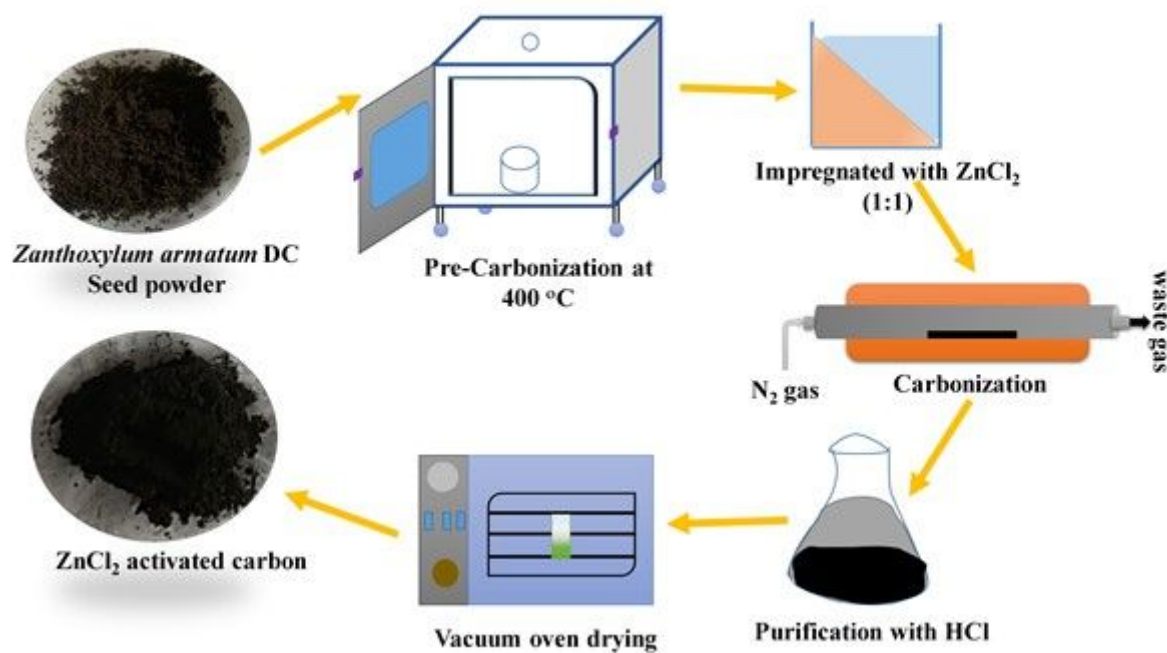


Figure 1

Schematic drawing for the synthesis of ZnCl₂ activation of carbon (ZAC)

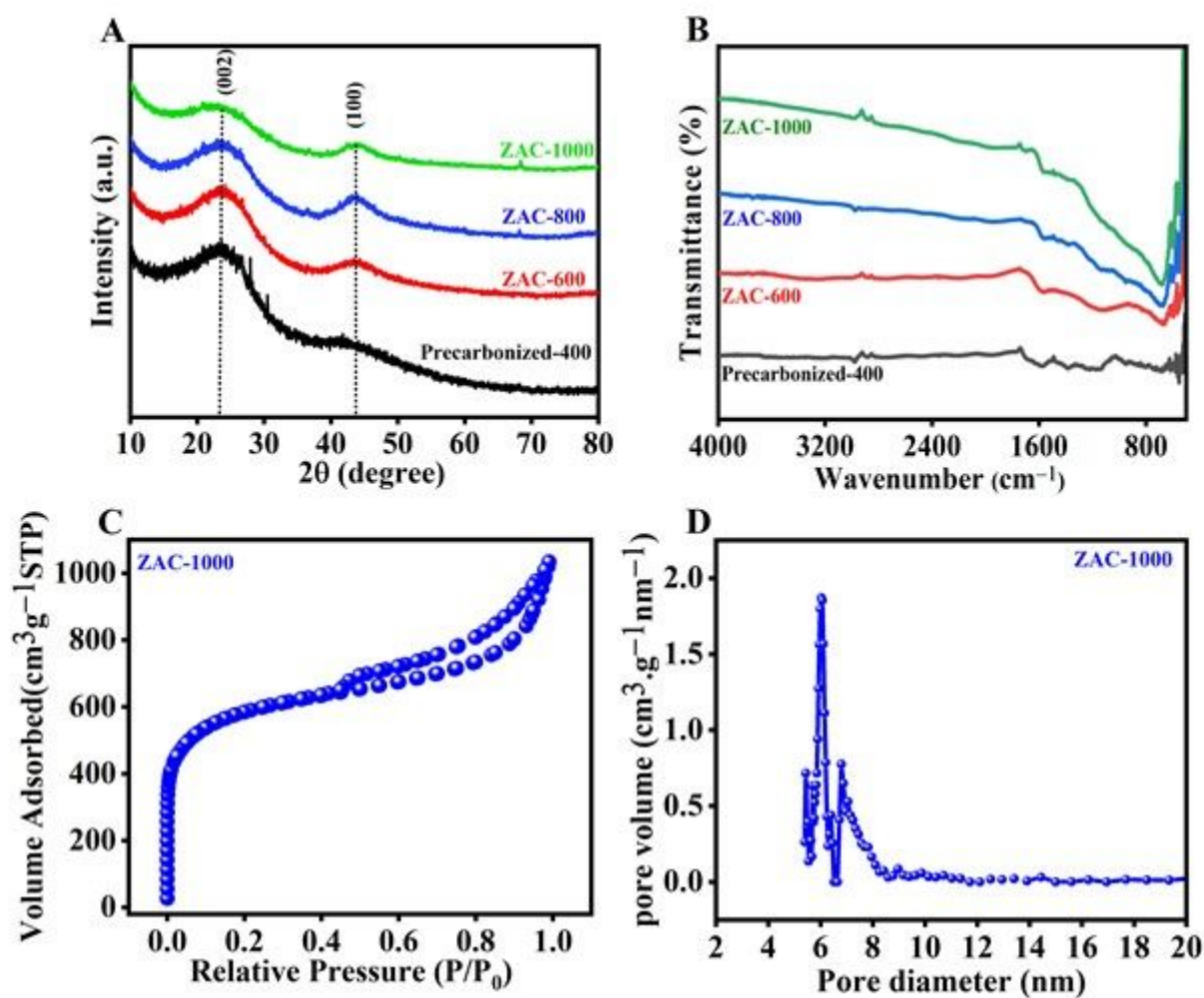


Figure 2

Physicochemical characterization: (A) XRD, (B) FTIR analysis of precarbonized-400, ZAC-600, ZAC-800 and ZAC-1000 sample (C) N_2 -adsorption-desorption isotherm, and (D) pore size distribution of ZAC-1000 sample.

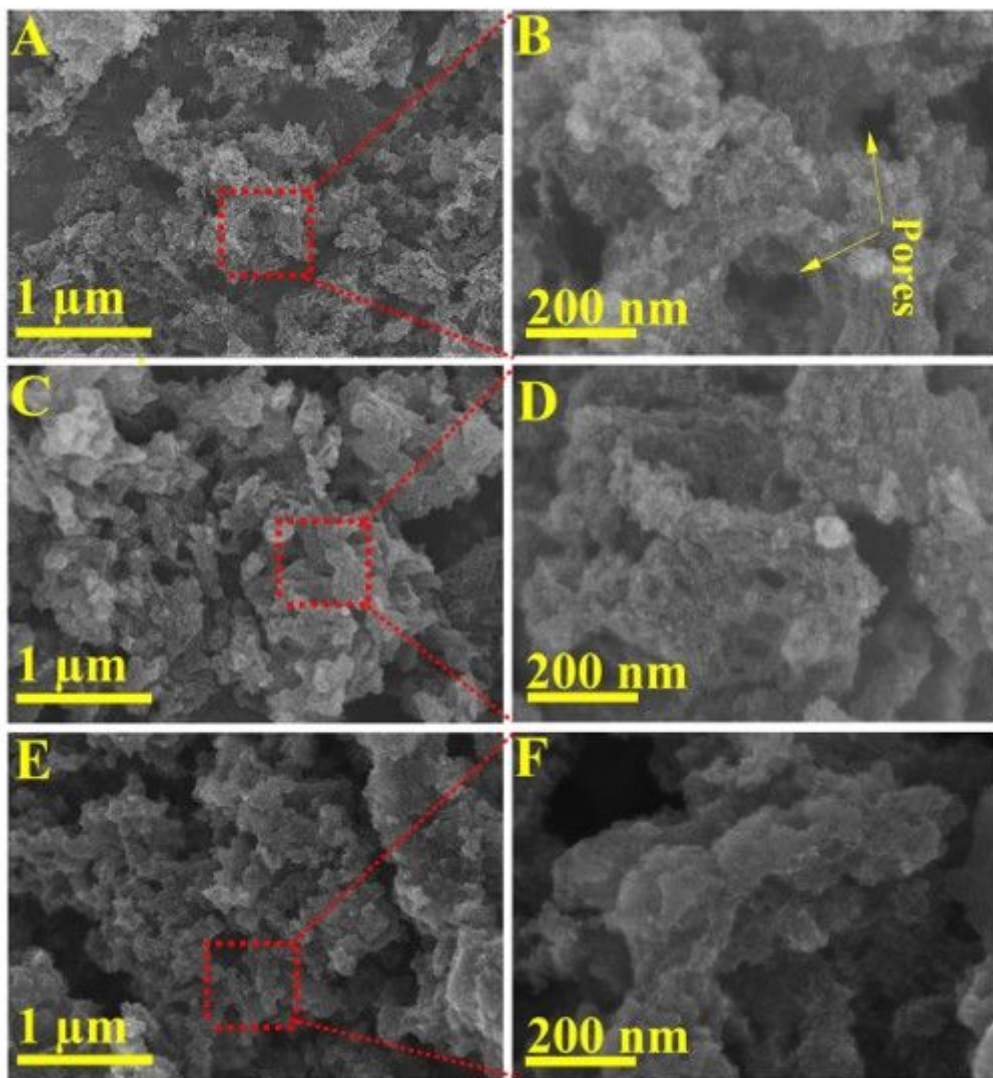


Figure 3

Surface morphology of activated carbon: High and low magnification FESEM image of (A, B) ZAC-1000, (C, D) ZAC-800 and (E, F) ZAC-600

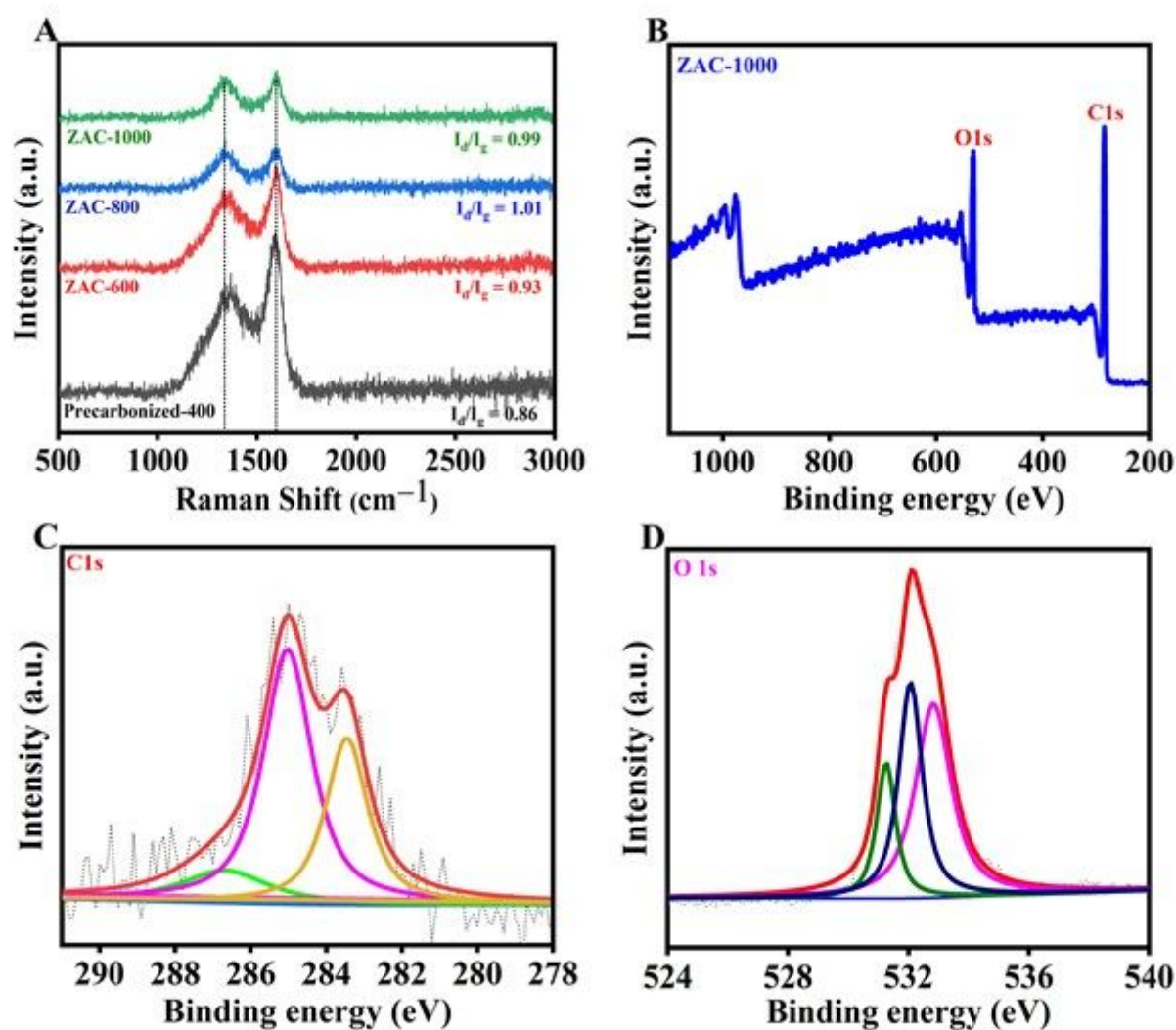


Figure 4

(A) Raman spectrum of ZAC-1000, ZAC-800, ZAC-600 and precarbonized-400 (B) The XPS survey analysis of ZAC-1000 and (C, D) represent the high resolution deconvoluted spectrum of C1s and O1s, respectively.

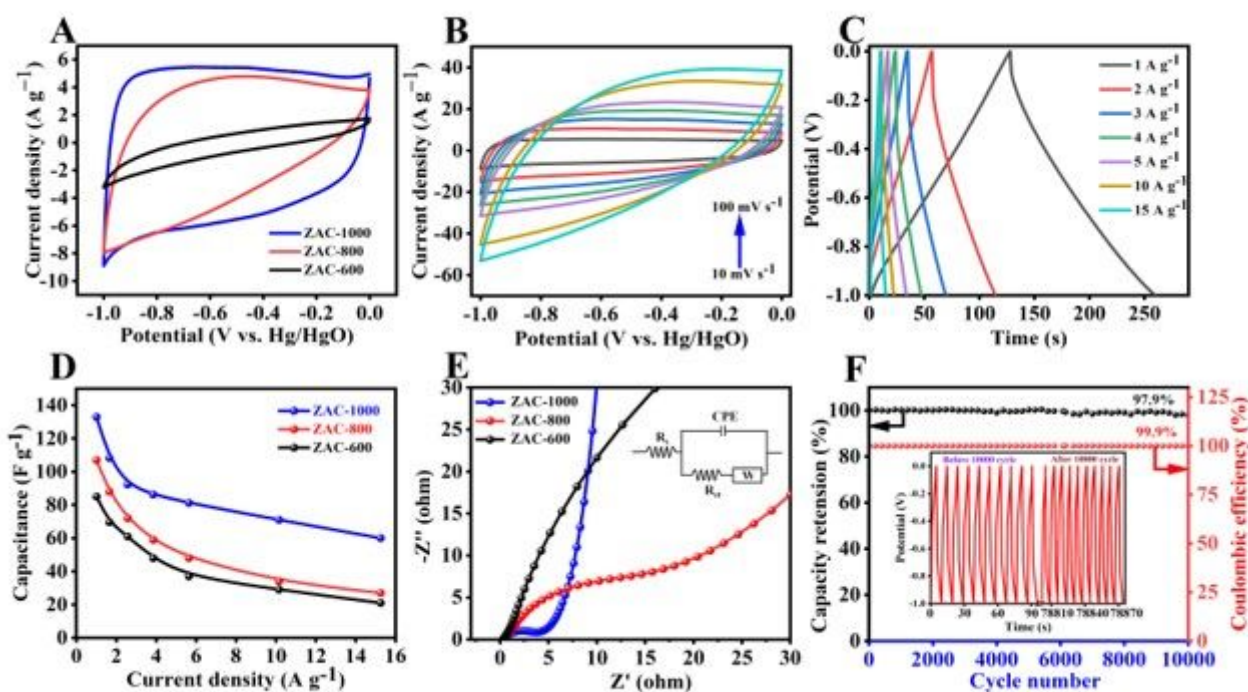


Figure 5

Electrochemical characterization: (A) CV plots of ZAC-1000, ZAC-800 and ZAC-600 at 10 mV s⁻¹ (B) CV plot of ZAC-1000 at various scan rate from 10 to 100 mV s⁻¹ (C) galvanostatic charge-discharge plot of the ZAC-1000 electrode at various current density (1-15 A g⁻¹) (D) capacitance vs. current density plot of ZAC-1000, ZAC-800 and ZAC-600 electrodes (E) EIS spectra of the ZAC-1000, ZAC-800 and ZAC-600 (F) cyclic stability and Coulombic efficiency of ZAC-1000 sample at current density 15 mV s⁻¹ (the inset displayed the first and last ten cycles of the GCD plot of 10,000 cycle)

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- [Supplementarymaterials20240123.docx](#)