Rice Husk-Derived Mesoporous Silica Nanostructure for Supercapacitors Application: a Possible Approach for Recycling Bio-Waste into a Value-Added Product

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Abstract
We synthesized mesoporous SiO\textsubscript{2} nanomatrix using rice husks as a precursor through a facile thermal combustion process. XRD, FTIR, EDX, and TEM analyses were used to validate the produced mesoporous SiO\textsubscript{2} nanomatrix. Electrochemical measurements were used to determine the specific capacitance of mesoporous SiO\textsubscript{2} nanomatrix, and the results showed that the specific capacitances are 216, 204, 182, 163, 152, 142, 135, 133, 124.4, 124 F/g at current densities of 0.5, 1, 2, 4, 6, 8, 10, 12, 14, and 16 A/g. The benefit of impurities, as well as the large surface area and mesoporous structure of rice husk derived SiO\textsubscript{2} nanostructures, allow Faradaic redox reactions at the electrode surface and the resulting supercapacitive behavior. This research might lead to a low-cost technique of producing supercapacitor electrodes using rice husk-derived SiO\textsubscript{2} as a precursor.

Keywords Rice husk · SiO\textsubscript{2} · Mesoporous · Nanomatrix · Supercapacitor

1 Introduction
Nanomaterials are known for their unique properties due to quantum confinement effects, high surface-to-volume ratio, and tunable properties. Interestingly, nanoscale research has been applied to various fields of science and technology [1–4]. Electrochemistry is one of the most notable applications of nanotechnology since the characteristics of nanoparticles influence their electrochemical properties as well as redox reactions on their surfaces [4–8]. The electron-transfer reaction occurs at the nanoscale level and the ability to control matter at the nanoscale is expanding and provides opportunities for a vast variety of applications. The applications of nanotechnology in electrochemistry are wide: from energy storage to biosensing [7–10].

Environmental concerns and demand for sustainable energy have prompted researchers to develop advanced energy storage systems. Supercapacitors are pioneering energy storage technology in recent decades owing to high power density, fast charge/discharge rates, high storage capacity, reliability, and extended life period [11, 12]. Its unique characteristics find applications in hybrid...
electric vehicles, regenerative breaking, flashlights, smartphones, electric tools, consumer electronics, memory devices, energy harvesting devices, etc. [11, 12]. Mesoporous characteristics, specific surface area (SSA), and charge transport available at the electrode have a part in the storage of charges, therefore they are key factors to the performance of the supercapacitors [13, 14]. In the past few decades, nanotechnology has become a driving force in materials research, leading a breakthrough revolution in the discovery of potential materials with improved efficiency for supercapacitor applications [13]. To develop supercapacitors with improved performance, numerous nanostructured materials including metal-organic frameworks, metal oxides, metal nitrides, carbon-based material, conducting polymers, and so on have been investigated [13, 14]. Recently, silica (SiO₂) nanoparticles have gained a lot of interest as a possible choice for constructing supercapacitor electrodes owed to advantages like non-toxicity, mesoporous structure, exceptional surface chemistry, and large SSA [15, 16]. However, the use of SiO₂ nanoparticles as supercapacitor electrodes has been limited due to poor electron transport processes caused by low conductivity [17]. As a result, few works have already been done towards integrating conductive components into SiO₂ nanostructures to improve their electrochemical characteristics [18–20]. Ali et al. used the citrate–gel technique to integrate Co₃O₄ into a SiO₂ framework and developed an electrode for supercapacitor [19]. By creating oxygen vacancies in SiO₂ nanostructures, Joshi et al. presented a simple approach to obtain electrodes with better electrochemical performance [21]. Vijayan et al. improved the redox performance of SiO₂ matrix by incorporating silver nanoparticles as an electrochemically active element [22]. SnO₂ decorated SiO₂ offer the supercapacitor electrode materials with a capacitance of about 448 F/g at 1 A/g current density [18]. Also, MnO₂ decorated mesoporous silica [23], SiO₂@C/TiO₂ hollow spheres [24], silica wrapped with graphene oxide-PANI [25] and sulfonated silica [26] have been investigated for supercapacitor applications.

Recently, researchers have become increasingly interested in developing silica nanoparticles from biowaste, which are non-toxic, readily available, and relatively inexpensive [16]. Rice husk proved to be a suitable alternative to synthetic SiO₂ precursors as a sustainable source of amorphous SiO₂. Rice husk is dumped as biowaste by a lot of rice milling factories, and approximately 100 million tonnes of rice husk are processed each year worldwide and a small proportion is employed for livestock feed [16, 27, 28]. In recent years, there has been a lot of interest in recycling rice husk waste into useful materials from the perspective of both environmental and economic concerns [16, 28]. Thanks to rice husk-derived SiO₂, which contains CaO, MgO, and K₂O, as well as a few trace elements that may play an important role in electro-chemical performance with advantage of the mesoporous structure and high SSA [16, 28]. Here, the feasibility of rice husk-derived SiO₂ as an electrode material for supercapacitor application is being investigated which may find a new platform for the development of cost-effective energy storage devices.

### 2 Experimental Methods

Utilizing rice husk as a starting material, a simple thermal combustion technique was employed to produce mesoporous SiO₂ nanomatrix. In a nutshell, an appropriate quantity of rice husk was purchased from a rice processing industry at Tiruchengode, Tamil Nadu, India, and they were washed thoroughly using water to flush away impurities and then dehydrated for 10 h at 110 °C. Thereafter, 15 g dehydrated rice husk was put into an alumina crucible and placed into a muffle furnace for thermal combustion. The thermal treatment process of rice husk was done for 5 h at 600 °C. After combustion, the obtained white color ash was cooled down to room temperature and stored in a desiccator at room temperature for further characterization. The schematic representation for the synthesis of silica from rice husk as a source is shown in Fig. 1.

X-ray diffraction (XRD) data were collected with 0.05° step size over 2θ range of 20–100 degree using Cr Kα radiation (λ = 2.2909 Å) in a Difray-401 X-ray diffractometer. Using the KBr pellet technique, the absorption of IR by the sample over the wavenumber of 4000–400 cm⁻¹ was measured using Nicolet 380 Fourier transform infrared (FTIR) spectrometer to identify the functional groups. Elemental mapping was done using a Tescan Vega 3 scanning electron microscope (SEM) equipped with an energy-dispersive X-ray (EDX) microanalyzer. A JSM JEOL-2100 transmission electron microscope (TEM) was used to investigate the selected area electron diffraction (SAED) and morphological features. A Quantachrome Nova 1200e analyzer was used to collect a N₂ adsorption-desorption behavior. Based on N₂ adsorption-desorption, the Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) approaches were employed to identify the SSA, pore size, and distribution. Physisorption of a gas molecule on a sample is the subject of the Brunauer–Emmett–Teller (BET) theory [29], which provides an analytical method to calculate the specific surface area of materials. To measure specific surface areas, BET theory can be applied to multilayer adsorption systems using a N₂ gas as adsorbate on the sample. The relation between the relative pressure of the adsorbate, and the amount of adsorbed gas can yield the below linear equation
\[
\frac{P}{v (P_0 - P)} = \frac{1}{v_m c} + \frac{(c - 1) P}{v_m c P_0}
\]

where \(v_m\) is the monolayer capacity and \(c\) is a constant associated with the energy of adsorption. By relating the relative pressure \(P/P_0\) to the left side of the equation above, specific surface area can be determined using the slope and intercept. To determine the pore size and volume of the prepared sample, the Barrett–Joyner–Halenda (BJH) technique was utilized [30]. The adsorption and desorption branches of \(N_2\) isotherms, as well as the hysteresis between them, provide information on the pore size, volume, and area.

The electrochemical characteristics of the synthesized sample were investigated at room temperature using a BioLogic SP-150 research-grade electrochemical analyzer controlled by EC-Lab® software-assisted computer. Platinum wire counter electrode, Ag/AgCl reference electrode, and 3 M KOH electrolyte were employed to analyze the electrochemical characterization of the sample coated Ni foam electrode. The sample coated Ni foam electrode was employed as a working electrode which was prepared using the mixture of 80 wt.% of the sample, 10 wt.% of polyvinylidene fluoride, 10 wt.% carbon black, and 2 mL of ethanol. The electrochemical characteristics of the synthesized sample were investigated at room temperature using a BioLogic SP-150 research-grade electrochemical analyzer controlled by EC-Lab® software-assisted computer. Platinum wire counter electrode, Ag/AgCl reference electrode, and KOH electrolyte were employed to analyze the electrochemical characterization of the prepared sample coated Ni foam electrode. The sample coated Ni foam electrode was employed as a working electrode which was prepared using the mixture of 80 wt.% of the sample, 10 wt.% of polyvinylidene fluoride, 10 wt.% carbon black, and 2 mL of ethanol. The cyclic voltammetry (CV) and galvanostatic charge/discharge (GCD) curve of the synthesized \(\text{SiO}_2\) sample as the working electrode was recorded. Using galvanostatic charge and discharge, the specific capacitances \((C_s)\) of synthesized \(\text{SiO}_2\) electrodes were calculated using the following equation [18, 22].

\[
C_s = \frac{I \Delta t}{m \Delta V}
\]

Here \(\Delta t\) denotes a period of discharge (s) and \(\Delta V\) denotes the electrochemical potential window, I represent the charge-discharge current (A) and \(m\) indicates the mass of sample on working electrode (g).

### 3 Results and Discussion

Figure 2(a) shows the XRD profile of the prepared rice husk ash, which displays a wide diffraction peak around 2\(\theta\) of 25–40° and it is attributed to (101) Miller plane. The X-ray diffraction peak reflects the poor crystalline nature of the sample [31]. Hence, the rice husk ash is composed of the poorly crystalline \(\text{SiO}_2\) (nearly amorphous state) and it is consistent with previous research [18, 22, 32]. The FT-IR spectrum of prepared rice husk ash is shown in Fig. 2(b). Due to symmetric stretching, asymmetric stretching, and bending vibrations of the O–Si–O functional group, the FTIR spectrum of the prepared rice husk ash displays peaks at 786 cm\(^{-1}\), 1160 cm\(^{-1}\), and 447 cm\(^{-1}\), respectively which further reveals synthesized
Rice husk ash is constituted of SiO$_2$ [18, 32–34]. The elemental mapping of the rice husk-derived SiO$_2$ is shown in Fig. 2(c), which depicts the distribution of silicon (37.7%), oxygen (50.5%), and impurities such as Zn (1.2%), Fe (1.6%), Ca (1.1%), K (1.4%), P (1.9%), Mg (0.9%), Cl (1.3%), and C (2.4%). Depending on the production methodologies, rice husk-derived SiO$_2$ may contain impurities such as sodium, carbon, iron oxide, potassium, calcium oxide, and magnesium oxide [16, 33]. To remove these impurities and produce pure SiO$_2$, pre-treatment and post-treatment procedures have been applied successfully [16, 33, 35]. In this work, we ignored pre-treatment and post-treatment processes to produce SiO$_2$ with impurities that may enable charge transport in a suitable electrolyte. The SAED pattern is shown in Fig. 2(d) demonstrates the poorly crystalline nature of the prepared SiO$_2$ which was corroborated with the XRD results. The diffraction ring around the white spot is attributed to the (101) Miller plane which is corroborated with XRD results.

Figure 3(a-c) shows the typical SEM and TEM observation. According to SEM and TEM investigations, thermal combustion of rice husk yields porous SiO$_2$ nanomatrix. To prepare spherical SiO$_2$ nanoparticles, rice husk is typically heated to 400–500 °C [18]. The porous SiO$_2$ nanomatrix was formed in this work was owing to the fusing of SiO$_2$ particles in rice husk at 600 °C. The topological properties found in this study potentially fulfill the fundamental needs of material applicable for supercapacitor applications [15–17].

The N$_2$ adsorption/desorption curve of the prepared SiO$_2$ nanomatrix is shown in Fig. 3(d). The observed hysteresis loop belongs to type IV isotherm indicating that the synthesized sample has mesoporous properties. The prepared SiO$_2$ nanomatrix has a SSA of 36.954m$^2$/g, according to BET analysis. The BJH analysis revealed that the sample exhibit a cumulative pore volume of 0.094cm$^3$/g with median pore sizes of 0.094cm$^3$/g.

Figure 4(a) shows the CV plot at a different rate of scanning with an applied potential of 0–0.5 V. The prepared SiO$_2$ exhibits strong symmetrical oxidation-reduction peaks which are owing to the well-defined Faradaic redox process that occurs at the interface of electrolyte-electrode. It indicates the excellent supercapacitive behavior of the prepared SiO$_2$-coated electrode. With the increase of sweep rate of 5-50 mV/s, the peak intensities owing to oxidation/reduction move in the direction of positive and negative potentials in the CV characteristic curve. These findings indicate that the Faradaic redox reaction is mediated by ion diffusion at the interface of electrolyte-electrode and impurities play an important role in the electron transport [22].

Figure 4(b) depicts the charge-discharge curve at current densities ranging 0.5–16 A/g. The charge-discharge curves were observed to be symmetric. It further corroborates the supercapacitance activity of rice husk-derived SiO$_2$ due to Faradaic redox processes. The specific capacitances are found to be 216, 204, 182, 163, 152, 142, 135, 133, 124.4, 124F/g at
Fig. 3 (a) SEM, (b-c) TEM, and (d) N₂ adsorption/desorption curve of the prepared SiO₂ nanomatrix

Fig. 4 (a) CV plot, (b) charge-discharge curve, and (c) specific capacitance of the prepared rice husk-derived SiO₂ as a working electrode
current densities of 0.5, 1, 2, 4, 6, 8, 10, 12, 14, and 16 A/g (Fig. 3(c)). The impurities in rice husk-derived SiO$_2$ nanomatrix, SSA, and mesoporous structure can facilitate the adsorption/desorption charges and make it possible to store the charges. Only very few reports are available on rice husk-derived silica nanoparticles for supercapacitor applications [18, 22]. By introducing silver nanoparticles as an electrochemically active material, Vijayan et al. prepared silver integrated rice husk silica nanostructure with the capacitance of 580 F/g at 1 A/g current density [22]. Also supercapacitor electrode materials with the capacitance of 448 F/g at 1 A/g current density have been prepared by decorating SnO$_2$ nanoparticles on rice husk-derived SiO$_2$ [18]. In this study, we have obtained materials with the capacitance of 216 F/g without incorporating any conductive element and it can be cost-effective material for the future application.

We investigated the electrochemical impedance of prepared mesoporous SiO$_2$ nanomatrix at frequencies ranging from 0.01 Hz to 100 kHz. The observed Nyquist plot is depicted in Fig. 5(a) which revealed a semi-circle at high frequencies, with a linear slope at low frequencies. An inset in Fig. 5(a) depicts the corresponding circuit that demonstrates the capacitive behavior and ion diffusion characteristics of the prepared mesoporous SiO$_2$ nanomatrix coated on a working electrode. Figure 5(b) shows how the prepared mesoporous SiO$_2$ nanomatrix has been able to maintain capacitance retention and Coulombic efficiency. After 1000 cycles, the Coulombic efficiency was found to be 89% which demonstrates that there is no counter-ion drain effect and no erosion takes place at the surface of the working electrode [22]. The inset in Fig. 5(b) indicates the working electrode coated with the prepared sample exhibit good stability up to 1000 cycles.

4 Conclusion

Using biowaste as a precursor, we produced a mesoporous SiO$_2$ nanomatrix via a simple thermal combustion technique. XRD, FTIR and EDX studies confirm that the prepared rice husk ash is amorphous silica with trace elements such as Zn, Fe, Ca, K, P, Mg, Cl and C. BET analysis. BET analysis revealed that the prepared SiO$_2$ nanomatrix has a SSA of 36.954 m$^2$/g with mesoporous characteristics. The impurities, SSA, and mesoporous structure of rice husk-derived SiO$_2$ nanomatrix enable Faradaic redox reactions and result in supercapacitive activity which corroborates the feasibility of rice husk-derived SiO$_2$ as an electrode material for supercapacitor application. This investigation may find a new platform for the development of cost-effective energy storage devices.

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Authors’ Contributions P. Araichimani: Conceptualization, Investigation, Methodology, Writing - Original Draft. K.M. Prabu: Supervision. G. Suresh Kumar: Validation, Writing-Review & Editing. Gopalu Karunakaran: Visualization, Formal analysis. S. Surendhiran: Characterization of materials. Mohd. Shkir: Characterization of material. S. AlFaify: Characterization of material.

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Data Availability Data and materials will be made on request.

Declarations

Ethics Approval Not applicable

Consent to Participate Not applicable.

Consent for Publication Not applicable.

Informed Consent Not applicable.

Research Involving Human Participants and/or Animals Not applicable.
Conflicts of Interest  Authors declare no conflict of interest.

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