



Green synthesis of Mn_3O_4 nanomaterials by *Cassia tora* leaves extract for supercapacitor device with activated carbon

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Abstract

The sustainable and eco-friendly approach was employed for the synthesis of manganese oxide (Mn_3O_4) nanomaterials with *Cassia tora* leaf extract as a natural reducing and stabilizing agent. The green-synthesized Mn_3O_4 nanoparticles exhibited a spongy and granular morphology, as confirmed by SEM and TEM analyses, with an average particle size of 21 nm, promoting efficient electrolyte ion diffusion. The Mn_3O_4 electrode, tested in 1 M KOH electrolyte, delivered remarkable pseudocapacitive performance with a specific capacitance of 468 F/g at 5 mV/s from CV analysis and 249 F/g at 3 A/g from GCD measurements. The capacitive behavior was governed by a diffusion-controlled charge storage mechanism, as supported by kinetic separation studies. The asymmetric solid-state supercapacitor device (ASSD) (Mn_3O_4 ||1M PVA-KOH||AC) exhibited a high energy density of 98 Wh/kg and a power density of 2064 W/kg, with outstanding cyclic stability, retaining 97.6% of its capacitance after 10,000 cycles. Electrochemical impedance spectroscopy revealed a low equivalent series resistance (ESR) of 3.5 Ω , highlighting excellent conductivity and electrode-electrolyte compatibility. The successful fabrication and integration of green Mn_3O_4 nanomaterials into a high-performance supercapacitor device underscore their potential in next-generation, sustainable energy storage systems.

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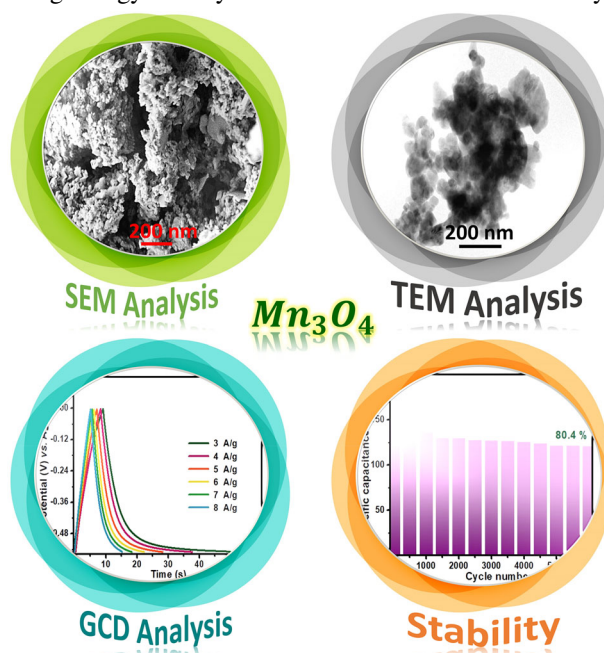
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Graphical Abstract

Green synthesis of Mn_3O_4 nanomaterials with *Cassia tora* extract for next-gen supercapacitor application is explored. Structural and morphological features confirm spongy, granular nanostructure with 21 nm size. Electrochemical tests reveal high specific capacitance, excellent rate performance, and 97.6% cycling retention. An eco-friendly (Mn_3O_4 ||1M PVA-KOH|AC) device delivers 98 Wh/kg energy density with low ESR and robust stability.



Keywords Mn_3O_4 · Nanomaterial · Green synthesis · Supercapacitor · Electrode · Asymmetric device

Highlights

- Green synthesis of Mn_3O_4 using *Cassia tora* leaf extract.
- Spongy granular nanostructure for rapid ion transport.
- High Cs of 468 F/g (CV) and 249 F/g (GCD).
- Diffusion-controlled pseudocapacitive behavior.
- ASSD device delivering 98 Wh/kg energy density.
- Excellent stability with 97.6% retention over 10,000 cycles.

1 Introduction

The global transition towards sustainable and renewable energy sources has amplified the demand for efficient and environmentally friendly energy storage technologies. Among various energy storage systems, supercapacitors have emerged as promising candidates due to their rapid charge-discharge rates, high power density, long cycle life, and relatively simple architecture. The performance of supercapacitors is primarily governed by the nature of electrode materials [1–3]. In this context, transition metal oxides have garnered substantial attention, with manganese-based oxides, particularly manganese (II, III) oxide (Mn_3O_4), standing out due to their excellent redox activity, structural tunability, natural abundance, and environmental

benignity [4–7]. The Mn_3O_4 possesses a mixed valence state ($\text{Mn}^{2+}/\text{Mn}^{3+}$), which enables rich Faradaic reactions, making it an ideal candidate for pseudocapacitive behavior. Its high theoretical specific capacitance (Cs), cost effectiveness, and favorable electrochemical stability contribute to its potential in energy storage devices, especially when configured in asymmetric supercapacitors that combine both high energy density (ED) and power densities (PD) [8–10].

Recent advancements in nanotechnology have shown that the nanoscaling of Mn_3O_4 particles significantly enhances surface area, ion diffusion kinetics, and charge storage capabilities [4, 11]. The nanostructured Mn_3O_4 materials offer abundant electroactive sites and shorter ion diffusion pathways, which are vital for high-rate charge-discharge performance. Various morphologies such as nanorods, nanoflakes,

and spherical nanoparticles have been synthesized using conventional chemical or hydrothermal methods. These approaches often involve toxic reagents, high energy consumption, and post-synthesis environmental risks [12–14]. To overcome these limitations, the focus has shifted toward green synthesis strategies using biological resources, which offer a cleaner, safer, and more sustainable alternative. The green synthesis route not only reduces the ecological footprint but also promotes the incorporation of bioactive phytochemicals that can serve as reducing, capping, and stabilizing agents during nanoparticle formation. Among natural bio resources, *Cassia tora* leaves are rich in flavonoids, phenolics, sterols, and Tannins, which play a crucial role in controlling the nucleation and growth of nanostructures through redox and complexation mechanisms [15, 16].

The utilization of *Cassia tora* leaf extract as a biogenic reagent for the synthesis of Mn_3O_4 nanoparticles presents a novel, eco-conscious approach to material fabrication. The phytochemicals within the extract offer a dual function, firstly acting as reducing agents to convert manganese salts into Mn_3O_4 nanomaterial, and secondly as stabilizing agents to prevent agglomeration and tailor the particle size and morphology. This biotemplate-assisted synthesis provides a low-cost, low-temperature, and non-toxic route for nanoparticle development [17, 18]. The green synthesis method aligns with the principles of green chemistry and sustainable engineering, mitigating the reliance on hazardous chemicals while achieving high purity and crystallinity in the final product. The tetragonal crystal structure of Mn_3O_4 plays a crucial role in enhancing its electrochemical performance, particularly for supercapacitor applications. The Mn_3O_4 crystallizes in a tetragonal phase (space group *I41/amd*), which accommodates both Mn^{2+} and Mn^{3+} ions in tetrahedral and octahedral coordination sites, respectively. This mixed valence configuration facilitates multiple redox transitions ($\text{Mn}^{2+}/\text{Mn}^{3+}$ and $\text{Mn}^{3+}/\text{Mn}^{4+}$), contributing to rich Faradaic charge storage [19]. The tetragonal symmetry also supports anisotropic ion diffusion pathways, enabling faster electron transport and better ionic conductivity compared to other crystal systems like cubic or orthorhombic. Its structural stability under repeated charge-discharge cycles enhances the long-term cycling performance of the electrode. Thus, the tetragonal phase offers a synergistic balance of structural integrity, electrochemical activity, and redox reversibility, making it highly suitable for high-performance energy storage devices [20].

The superior redox properties of Mn_3O_4 and the sustainable benefits of green synthesis, the present work aims to explore the potential of Mn_3O_4 nanomaterials synthesized with *Cassia tora* extract for application in asymmetric supercapacitor devices. Asymmetric configurations offer an advantage over symmetric counterparts by extending the voltage window, thus enhancing the overall energy density

without compromising the power output [21]. In this study, the electrochemical behavior of the green-synthesized Mn_3O_4 electrode was systematically evaluated using cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), and electrochemical impedance spectroscopy (EIS). The green synthesis of Mn_3O_4 nanomaterials using *Cassia tora* leaf extract as a natural reducing and stabilizing agent, thereby eliminating the need for hazardous chemicals. Unlike earlier studies that focused only on Mn-based oxides or other plant-derived routes, our approach uniquely combines Mn_3O_4 with activated carbon to construct a functional supercapacitor device. The plant-mediated synthesis not only tailors the nanostructure but also provides a synergistic effect that enhances capacitance, rate capability, and cyclic stability. This specific strategy establishes an eco-friendly, low-cost, and sustainable route for fabricating high-performance Mn_3O_4 -based supercapacitor electrodes, setting it apart from previously reported methods [16].

2 Synthesis

2.1 Synthesis of aqueous leaves extract

The Fresh *Cassia tora* leaves were initially rinsed thoroughly using double-distilled water (DDW) to eliminate any surface impurities, followed by drying in a hot air oven at approximately 60 °C for 3–4 h. The dried leaves were then finely ground into a uniform powder using a mechanical grinder. Subsequently, 50 g of this powdered material was immersed in 500 ml of DDW and subjected to gentle heating on a magnetic stirrer hot plate, maintained at 40–50 °C for about 60 min to facilitate the extraction of bioactive compounds. The resulting solution was allowed to cool slightly before being passed through Whatman No. 1 filter paper to remove solid residues. The clear aqueous extract obtained was stored and directly employed in the green synthesis of Mn_3O_4 nanoparticles [22].

2.2 Synthesis of Mn_3O_4 nanomaterial

To initiate the green synthesis, 500 ml of freshly prepared *Cassia tora* leaf extract was slowly introduced into 50 ml of 0.1 M $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ aqueous solution under continuous stirring. Alternatively, a control reaction was also prepared using a 0.1 M $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solution with 500 ml of leaf extract to compare reaction efficiency. The reaction mixtures were maintained on a magnetic hot plate stirrer at a temperature range of 23–28 °C and stirred at a consistent speed of 500–700 rpm for approximately 4 to 5 h to facilitate nanoparticle formation through phytochemical-mediated reduction and stabilization. The resulting Mn_3O_4 nanomaterial was

separated and thoroughly rinsed with 50% ethanol solution to eliminate any residual organic impurities or unreacted biomolecules. The cleaned product was then allowed to dry naturally at ambient temperature for around 4 h. Finally, to enhance crystallinity and remove any remaining moisture or volatile components, the dried nanoparticles were subjected to thermal annealing at 350 °C in a muffle furnace, resulting in phase-pure Mn_3O_4 nanostructures suitable for electrode fabrication [22]. Regarding calcination, while higher temperatures are generally preferred for organic removal, our optimization confirmed that 350 °C was sufficient to decompose the residual organics from the *Cassia tora* extract while preserving the nanostructured morphology of Mn_3O_4 . This condition yielded well-crystallized materials with clean active sites, favorable defect chemistry, and enhanced electrochemical stability. The plant-mediated route promoted uniformly dispersed, high surface area nanostructures, facilitating rapid ion transport and improved capacitive performance [23].

2.3 Synthesis of activated carbon (negative) electrode

The activated carbon (AC) negative electrode was prepared by dissolving 1 g of polyvinyl alcohol (PVA) in 10 ml of deionized water under continuous stirring at 70–80 °C for 2–3 h to obtain a transparent and homogeneous polymer solution. A pre-weighed amount of activated carbon powder was then added to the PVA solution, and the mixture was stirred vigorously at the same temperature for an additional 2 h to achieve uniform dispersion of the carbon particles within the polymer matrix. The resulting black slurry was partially dried in a desiccator to adjust its viscosity for coating. This well-mixed AC-PVA paste was uniformly coated onto a thoroughly cleaned copper foil substrate ($15 \times 20 \text{ cm}^2$) using the doctor blade method to maintain consistent film thickness. The coated electrodes were first dried at 50–60 °C for 4 h and subsequently subjected to thermal treatment in a muffle furnace at 353 K (80 °C) for 6–7 h to improve film adhesion, mechanical stability, and structural integrity. The final AC-coated copper electrodes were uniform, crack-free, and employed as negative electrodes for the assembly of the solid-state asymmetric supercapacitor device [24].

2.4 Electrochemical measurements

Through the use of CV, GCD, and EIS, the electrochemical properties of Mn_3O_4 nanomaterial electrode were evaluated. The three-electrode cell design was employed to analyse electrochemical performance in a 1 M KOH solution, with Mn_3O_4 nanomaterial electrode, platinum, and Ag/AgCl helping as the working, counter, and reference electrodes, respectively. The charging-discharging behaviors at

numerous current densities in the same potential window were examined, and CV measurements were performed at various sweep speeds in the potential window of –0.55 to 0 V. With an alternative current amplitude of 10 mV and a bias potential of 0.55 V, EIS was analysed in the frequency range of 100 Hz to 10 kHz [24].

For a two-electrode supercapacitor device, a separator was sandwiched between two electrodes. In our case, the gel electrolyte works as both an electrolyte and a separator. Thus, the full cell was considered as the series combination of two capacitors. The total capacitance (C_{cell}) was calculated according to Eqs. 1–3, in which C_+ and C_- are the capacitances of the associated two electrodes [25].

$$\frac{1}{C_{\text{cell}}} = \frac{1}{C_+} + \frac{1}{C_-} \quad (1)$$

For a device system, $C_+ = C_- = C_{\text{electrode}}$.

So,

$$C_{\text{cell}} = \frac{C_{\text{electrode}}}{2} \quad (2)$$

Cell specific capacitance:

$$C_{\text{SP,cell}} = \frac{C_{\text{cell}}}{m_{\text{total}}} = \frac{C_{\text{electrode}}}{2} \times \frac{1}{2 \times m_{\text{electrode}}} = \frac{C_{\text{SP,electrode}}}{4} \quad (3)$$

where m_{total} specifies the total mass ($m_+ + m_-$) in the cell. As the cell configuration is symmetric, $m_+ = m_- = m_{\text{electrode}}$. Thus, $m_+ + m_- = 2 \times m_{\text{electrode}}$. Again, $C_{\text{SP,electrode}} = C_{\text{electrode}}/m_{\text{electrode}}$. Thus, it is obvious that the total specific capacitance of the cell (two electrode) will always be one fourth of the associated three electrode system [25]. (Note: Supplementary experimental procedures can be found in the Supporting Information. Section S1.1 provides an overview of materials used, while Section S1.2 details the preparation of the PVA gel. The fabrication process of the Mn_3O_4 electrode is described in Section S1.3, and the synthesis of the PVA-KOH solid-state electrolyte gel is outlined in Section S1.4. Section S1.5 includes complete information on the characterization techniques employed).

2.5 Fabrication of solid-state devices

The asymmetric supercapacitor device was fabricated using Mn_3O_4 as the positive electrode and activated carbon (AC) as the negative electrode. A solid-state PVA-KOH gel was employed as both the electrolyte and binder, while a thin filter paper (Whatman 41) served as the separator. Prior to assembly, both the positive and negative electrodes, along with the separator, were immersed in the PVA-KOH gel electrolyte for approximately 20 s to ensure thorough impregnation, followed by air drying at 30–40 °C for 1 h. Additionally, the Mn_3O_4 electrode was uniformly coated

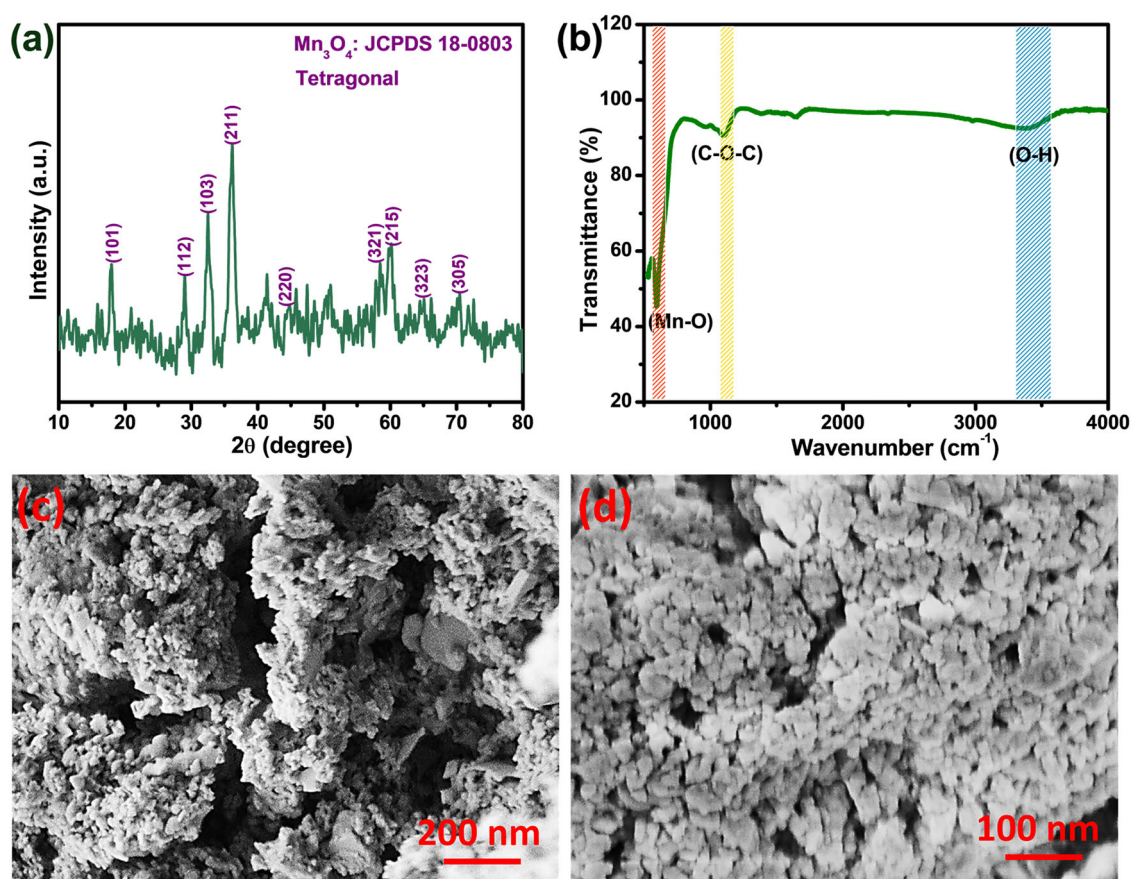


Fig. 1 **a** XRD patterns revealing the tetragonal crystal structure of Mn₃O₄ nanomaterial, **b** A FTIR spectra, SEM images of Mn₃O₄ nanomaterial at magnification of **c** 200 nm, **d** 100 nm

with a thin layer of the gel electrolyte and further dried in an electric oven at 30–40 °C for 7–8 h to remove residual moisture and improve interfacial adhesion. The final device was assembled by carefully sandwiching the gel-coated Mn₃O₄ and AC electrodes with the separator placed in between, followed by pressing the stacked layers firmly for 4–5 h. This process ensured intimate contact between the electrodes and electrolyte, thereby enhancing charge transport and improving the overall electrochemical performance of the solid-state asymmetric supercapacitor [24].

3 Results and discussions

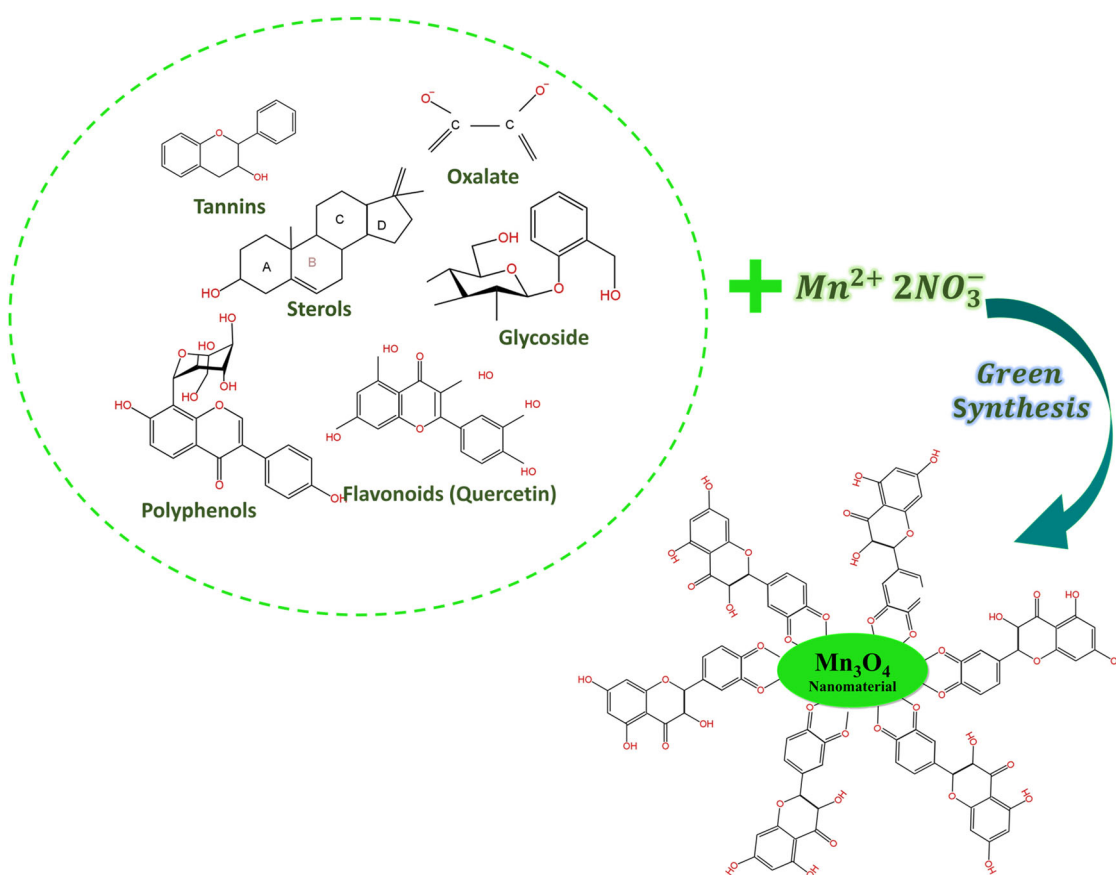
3.1 Reaction mechanism of Mn₃O₄ nanomaterial formation

The green synthesis of Mn₃O₄ nanoparticles using *Cassia tora* leaf extract proceeds with the help of a phytochemical-assisted redox pathway, where bioactive compounds such as polyphenols, flavonoids (quercetin), tannins, glycosides, sterols, and oxalates play integral roles in reducing Mn²⁺ ions and stabilizing the resulting

nanoparticles. Upon mixing Mn(NO₃)₂·6H₂O with the aqueous leaf extract, the hydroxyl and carbonyl groups from polyphenols and flavonoids donate electrons to Mn²⁺, oxidizing it to Mn³⁺ and enabling the formation of mixed-valence Mn₃O₄ nanostructures through a controlled nucleation and growth process [26, 27]. Though multiple phytochemicals are involved in this process, the schematic in Scheme 1 emphasizes only flavonoids capping in the final product to highlight their dominant role in nanoparticle stabilization due to their high electron-donating capacity and surface binding affinity.

3.2 X-ray diffraction analysis

The crystalline structure and phase purity of the synthesized Mn₃O₄ nanomaterial were systematically investigated using XRD, as presented in Fig. 1(a). The XRD pattern reveals sharp and well-defined peaks, confirming the formation of highly crystalline Mn₃O₄. The observed diffraction peaks at 2θ values of approximately 17.8°, 29.0°, 32.5°, 36.2°, 44.7°, 58.5°, 60.2°, 65.1°, and 70.5° are distinctly indexed to the (101), (112), (103), (211), (220), (321), (215), (323), and (305) lattice planes, correspondingly, matching well



Scheme 1 The schematic diagram depicts the reaction kinetics for the synthesized Mn_3O_4 nanomaterial, highlighting the formation mechanism

with the standard JCPDS card no. 18-0803 [28, 29]. This pattern conclusively confirms that the synthesized Mn_3O_4 nanoparticles crystallize in a tetragonal structure, which is characteristic of high-purity Mn_3O_4 . The sharpness and intensity of the peaks indicate a high degree of crystallinity, which is crucial for efficient charge storage in supercapacitor electrodes. The average crystallite size (D), calculated using the Debye Scherrer equation, is found to be in the range of $\approx 20\text{--}25$ nm, suggesting the nanocrystalline nature of the particles [30]. Such fine crystallite dimensions contribute significantly to increasing the surface-to-volume ratio, which facilitates rapid ion diffusion and charge transfer at the electrode-electrolyte interface. The microstrain (ϵ) and dislocation density (δ) values are estimated to be 0.0472 and 8.37×10^{14} lines·m $^{-2}$, correspondingly, indicating moderate internal lattice strain and defect density. These defects may further contribute to enhanced pseudocapacitive behavior by providing more active sites for redox reactions [31]. (Note: The crystallite size (D), along with microstrain and dislocation density, was calculated using the Scherrer equation and related formulas, as detailed in Supporting Information Section S2.1.)

3.3 FTIR spectra analysis

The FTIR analysis of Mn_3O_4 , a distinct absorption band observed at 3376.82 cm^{-1} corresponds to the O-H stretching vibration, indicating the presence of hydroxyl groups, which may originate from polyphenols and flavonoids in the plant extract. The peak at 1098.15 cm^{-1} is attributed to C-O-C stretching vibrations, suggesting the involvement of ether or alcohol functional groups, commonly present in plant-derived phytochemicals. Additionally, the peak located at 595.01 cm^{-1} is assigned to the Mn-O stretching vibration, confirming the formation of manganese oxide nanoparticles in Fig. 1(b) [32, 33]. These functional groups not only confirm the successful capping and stabilization of Mn_3O_4 nanoparticles by bioactive compounds but also reflect the bio-reducing role of *Cassia Tora* extract in the synthesis process.

3.4 SEM analysis

The surface morphology and nanostructural features of the green-synthesized Mn_3O_4 nanoparticles were investigated using SEM images, as depicted in Fig. 1(c, d). The SEM

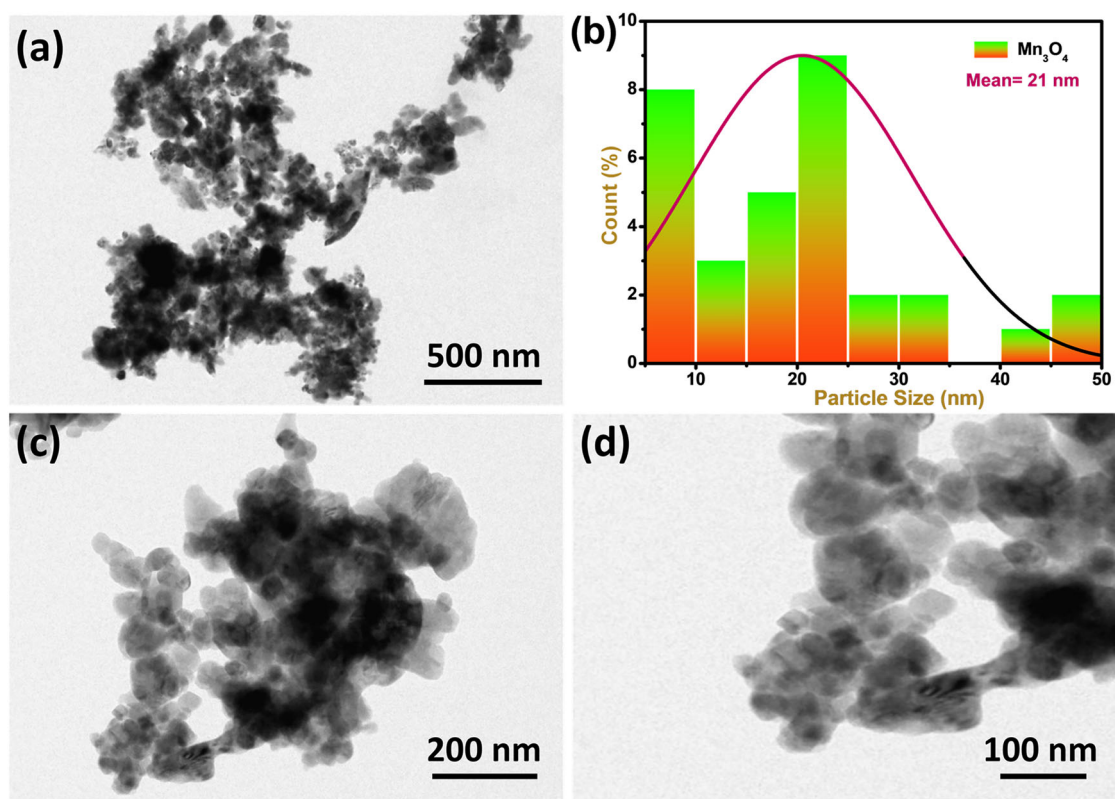


Fig. 2 **a** The TEM image at magnification of 500 nm, **b** Histogram of Mn₃O₄ nanomaterial, the TEM images at different magnification **c** 200 nm, and **d** 100 nm of Mn₃O₄ nanomaterial

images at different magnifications (200 nm and 100 nm scale bars) reveal that the Mn₃O₄ nanomaterials exhibit a distinct aggregated spongy granular morphology [34, 35]. This structure consists of densely packed nanograins forming clusters with abundant interparticle voids, which are advantageous for electrochemical applications as they provide enhanced surface area and facilitate easy electrolyte diffusion. The granular surface texture indicates successful nucleation and controlled growth of nanoparticles mediated by the phytochemicals present in the *Cassia tora* leaf extract. These bioactive molecules act as both reducing and stabilizing agents during the synthesis process, resulting in uniformly distributed nanosized particles with a loosely agglomerated network. The observed porous framework not only promotes better ion accessibility and electron transfer during charge-discharge cycles but also contributes to the structural stability of the electrode. Therefore, the granular porous morphology of Mn₃O₄ is highly beneficial for achieving improved electrochemical performance [4, 36, 37].

3.5 TEM analysis

The Transmission Electron Microscopy (TEM) analysis provides critical insights into the nanostructure and

morphology of the green-synthesized Mn₃O₄ nanoparticles using *Cassia tora* leaf extract. The low magnification TEM image in Fig. 2(a), clearly reveals the formation of loosely agglomerated, sponge like nanoparticle clusters, exhibiting a highly porous and granular morphology consistent with the surface features observed in SEM analysis. These agglomerates, composed of fine nanoscale particles, form a three-dimensional interconnected network that is beneficial for facilitating rapid ion diffusion and electrolyte accessibility [4, 38]. The particle size distribution histogram shown in Fig. 2(b) confirms a relatively narrow size dispersion, with an average particle diameter of approximately 21 nm, indicating controlled nucleation and uniform growth during the green synthesis process, likely aided by phytochemicals present in the *Cassia tora* extract acting as natural reducing and stabilizing agents. Higher resolution TEM images at 200 nm and 100 nm scales as shown in Fig. 2(c, d) reveal that the individual Mn₃O₄ nanoparticles possess semi-spherical to irregular shapes with well-defined edges and moderate agglomeration, signifying good crystallinity and phase purity. The nanoscale nature of these particles enhances the surface-to-volume ratio, which is a crucial factor in optimizing faradaic redox activity and charge storage capability.

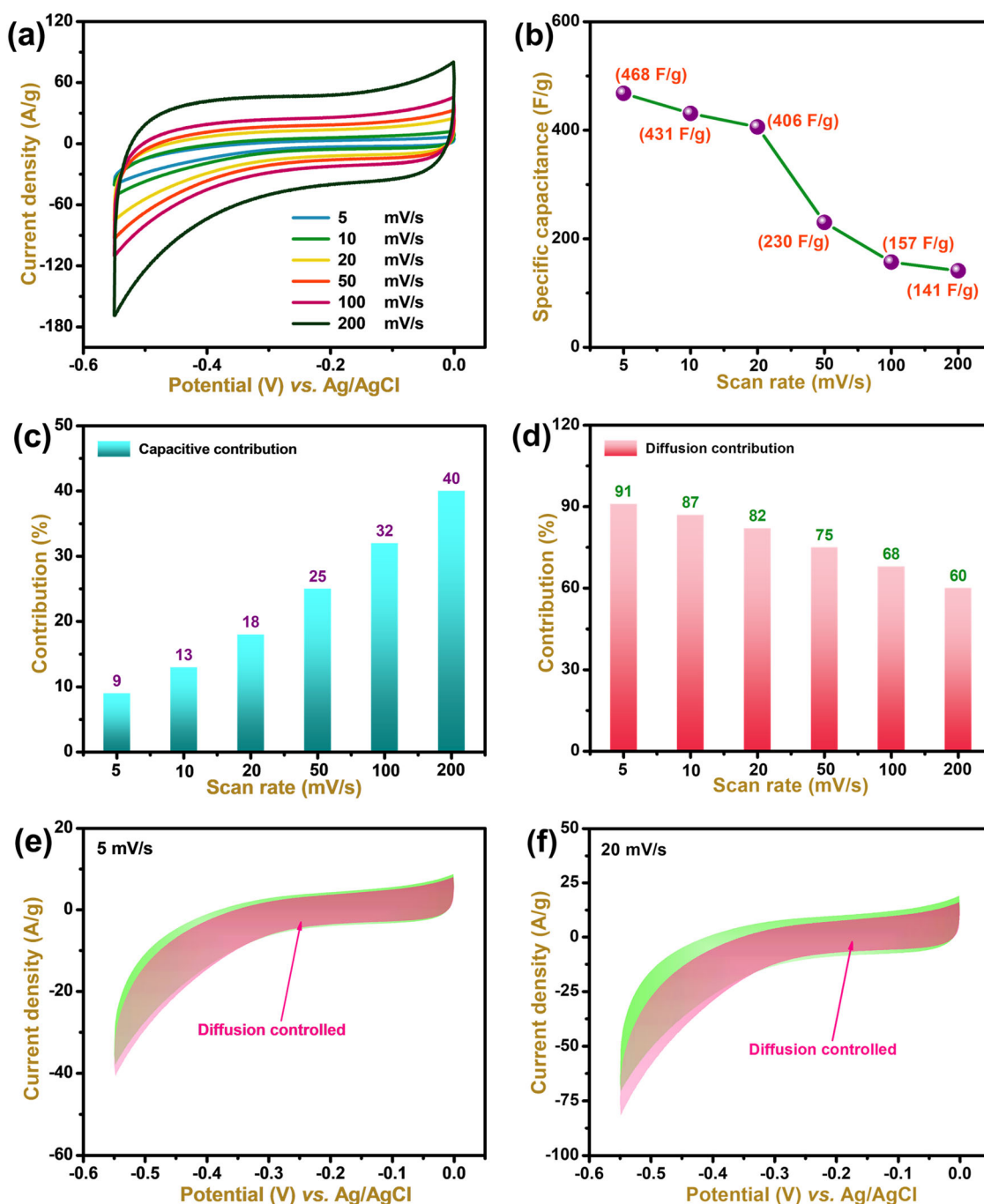


Fig. 3 **a** The CV curves of the Mn_3O_4 electrode recorded at different scan rates ranging from 2 to 100 mV/s, highlighting its electrochemical characteristics, **b** A Cs in F/g derived from CV data plotted against scan rates in mV/s, **c**, **d** Analysis of capacitive and diffusion-controlled

charge contributions across various scan rates, **e**, **f** Quantitative separation of capacitive and diffusion contributions at 5 and 20 mV/s, respectively

4 Supercapacitive analysis of the electrode

4.1 CV analysis

The CV profiles of the Mn_3O_4 electrode measured at different scan rates (5–200 mV/s) in 1 M KOH electrolyte

are presented in Fig. 3(a). The CV curves show distinct, well-defined redox peaks, clearly confirming the pseudo-capacitive behavior of the Mn_3O_4 electrode. The presence of broad anodic and cathodic peaks indicates reversible faradaic redox reactions involving the multivalent oxidation states of manganese [39]. While Mn_3O_4 is considered

Table 1 Comparison of the synthesized electrode (Mn₃O₄) performance with previously reported electrodes

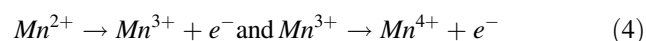
Sr. No.	Electrode material	Method	Electrolyte	Cs _(CV) (F/g)	Stability in %		Ref.
					Retention	No. of cycles	
1.	Mn ₃ O ₄	Chemical precipitation	1 M Na ₂ SO ₄	322	77	1000	[68]
2.	Mn ₃ O ₄	Dissolution, evaporation, and calcination	6 M KOH	667	71.8	1200	[69]
3.	Mn ₃ O ₄	Ultrasonic and hydrolyzation	1 M Na ₂ SO ₄	261	–	–	[70]
4.	Mn ₃ O ₄	Hydrothermal	2 M KOH	277	123	5000	[71]
5.	Mn ₃ O ₄ /rGO	Modified Hummers	1 M Na ₂ SO ₄	228	95	5000	[72]
6.	Mn ₃ O ₄ /graphene nanosheets	Ultrasound assisted	1 M Na ₂ SO ₄	312	76	1000	[73]
7.	graphene/Mn ₃ O ₄	Modified Hummers	1 M K ₂ SO ₄	260	94	1000	[74]
8.	Mn ₃ O ₄	Spray pyrolysis	1 M Na ₂ SO ₄	394	93.01	1000	[75]
9.	Mn ₃ O ₄ /rGO	Solvothermal	2 M KOH	947	88.1	4000	[76]
10.	Mn ₃ O ₄	Spray pyrolysis	0.1 M Na ₂ SO ₄	105.3 mF/cm ²	–	–	[77]
11.	Mn₃O₄	Green synthesis	1 M KOH	468	92.8	6000	Our work

The bold values indicate the best/maximum performance parameters obtained in this study

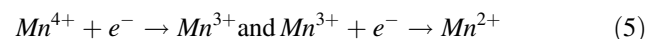
Cs_(CV) = Specific capacitance by cyclic voltammetry plots

a pseudocapacitive material due to its mixed valence spinel structure containing both Mn²⁺ and Mn³⁺, its cyclic voltammograms often do not display distinct redox peaks. Instead, the Mn₃O₄ electrode exhibits a quasi-rectangular CV profile that reflects capacitive-like behavior. This occurs because the redox processes are surface confined, highly reversible, and strongly overlapped across a broad potential window, which masks the appearance of individual peaks. As a result, the charge storage originates primarily from pseudocapacitance rather than well-defined faradaic transitions, a behavior consistent with earlier reports on Mn₃O₄-based electrodes [40, 41]. At lower scan rates, the peaks are more pronounced and symmetric, suggesting efficient charge transfer kinetics and full electrochemical utilization of the active material. As the scan rate increases, the CV curves maintain their shape with slight broadening and shifting of redox peaks, which is indicative of diffusion-controlled redox reactions and good rate capability [42]. The typical electrochemical reaction mechanism occurring in the alkaline medium can be expressed as follows:

4.2 Anodic reaction



4.3 Cathodic reaction



These reactions occur reversibly at the electrode surface during the forward and reverse potential sweeps. The transitions from Mn²⁺ to Mn³⁺ and then to Mn⁴⁺ during oxidation, and the reverse during reduction, correspond to the anodic and cathodic peaks observed in the CV plots. The peak separation remains relatively small even at high scan rates, indicating fast electron and ion transport within the Mn₃O₄ matrix. The good symmetry and quasi-rectangular shape at higher scan rates [43, 44]. A further signify superior capacitive reversibility and electrode stability, which are critical for high-performance energy storage in supercapacitor devices.

Figure 3(b) shows the variation of Cs as a function of scan rate, calculated from the CVs. The Mn₃O₄ electrode exhibits a maximum Cs of 468 F/g at 5 mV/s, which gradually decreases to 141 F/g at 200 mV/s. The synthesized electrode (Mn₃O₄) results are compared with previously reported electrodes in Table 1. This reduction in Cs with increasing scan rate is a typical trend observed in pseudocapacitive materials and can be attributed to limited ion diffusion and incomplete redox utilization at higher scan

rates [45]. At low scan rates, the electrolyte ions have sufficient time to diffuse deeply into the porous structure of the electrode and participate fully in the redox reactions, leading to higher capacitance values. At higher scan rates, only the outer surface of the electrode is accessible for charge storage, resulting in lower capacitance [46, 47]. The electrode maintains considerable capacitance even at high scan rates, indicating excellent rate capability and accessibility of redox-active sites due to the nanoscale morphology and porous network structure of the biosynthesized Mn_3O_4 nanomaterial. These results affirm the effectiveness of *Cassia tora*-mediated green synthesis in producing high-performance electrode materials suitable for next-generation energy devices. The Cs in F/g reflects the charge storage capability of the electrode material per unit mass and is a key performance parameter for supercapacitors. Higher values indicate more efficient utilization of active material, enabling lightweight and compact energy storage devices. In this work, our electrode exhibits competitive specific capacitance compared to reported systems, confirming its suitability for supercapacitor applications [48, 49]. (Note: The formulas used for calculating specific capacitance from CV and GCD data, along with the equations for energy density and power density, are provided in Supporting Information Section S2.2)

The charge storage performance of pseudocapacitive electrodes, such as those made from Mn_3O_4 electrode, is influenced by two key mechanisms. The first mechanism involves the diffusion of electrolyte ions into the electrode material, leading to reversible redox reactions at the active sites. The second mechanism is related to the capacitive behavior, which is driven by the adsorption and desorption of ions on the electrode's electroactive surface [50]. To more accurately determine the contribution of each mechanism to the overall capacitance of the Mn_3O_4 electrode, cyclic voltammetry curves were analysed to explore the relationship between the current response and the scan rate.

$$i = K_1 v + K_2 v^{1/2} \quad (6)$$

$$\frac{i}{v^{1/2}} = K_1 v^{1/2} + K_2 \quad (7)$$

The constants k_1 and k_2 , representing capacitive and diffusive contributions, respectively, can be determined from the slope and intercept of a linear plot of $i(V)/v^{1/2}$ vs. $v^{1/2}$. In this context, the slope corresponds to the capacitive current, while the y-intercept reflects the diffusive current [51]. For the Mn_3O_4 electrode, this $i(V)/v^{1/2}$ vs. $v^{1/2}$ plot was analysed to distinguish between the redox activity and capacitive behavior during the faradaic process, allowing for the calculation of the relative contributions of diffusion and capacitance.

To further understand the charge storage mechanism of the Mn_3O_4 electrode, the capacitive and diffusion-controlled contributions were analysed at different scan rates, Fig. 3(c) illustrates the capacitive contribution at various scan rates from 5 to 200 mV/s. It is evident that the capacitive charge storage increases progressively with scan rate, starting from 9% at 5 mV/s and reaching 40% at 200 mV/s. This increasing trend is attributed to the surface-controlled redox reactions dominating at higher scan rates, where the electrolyte ions interact primarily with the outer surface of the active material. At higher scan rates, electrolyte ions do not have sufficient time to diffuse into the inner pores of the electrode, resulting in greater reliance on surface capacitance rather than bulk redox reactions. This behavior is beneficial for high-power applications, as capacitive mechanisms support faster charge-discharge processes.

Figure 3(d) shows the diffusion-controlled contribution, which exhibits a decreasing trend with increasing scan rate. At 5 mV/s, diffusion contribution is dominant, accounting for 91% of the total current, which gradually declines to 60% at 200 mV/s. This confirms that at lower scan rates, the charge storage is primarily governed by faradaic redox reactions involving the bulk of the Mn_3O_4 electrode, where ions have adequate time to diffuse deep into the porous structure. The gradual transition from diffusion-dominated to capacitive-dominated behavior is characteristic of pseudocapacitive materials. Figure 3(e, f) further visualize the quantitative separation of diffusion and capacitive-controlled currents at 5 mV/s and 20 mV/s, respectively. The shaded regions in the CV profiles clearly demarcate the diffusion-controlled areas, which dominate at 5 mV/s and reduce at 20 mV/s. This shift reinforces that higher scan rates favor surface redox processes over deeper bulk diffusion. Inclusive, the synergistic coexistence of both charge storage mechanisms provides the Mn_3O_4 electrode with a balance of high energy and power densities, confirming its suitability for next-generation devices.

4.4 GCD and stability analysis

The GCD curves of the Mn_3O_4 electrode at current densities ranging from 3 to 8 A/g in a 1 M KOH aqueous electrolyte are shown in Fig. 4(a). The GCD profiles exhibit a nearly symmetrical triangular shape with minor deviation from linearity, indicating a pseudocapacitive charge storage behavior. This non-linearity is attributed to faradaic redox reactions of Mn ions, consistent with the CV results. As the current density increases, the discharge time decreases, which is typical due to limited time for ion diffusion and charge transfer [4, 52]. The longest discharge time observed at 3 A/g demonstrates maximum utilization of electrochemically active sites at low current densities. The exhibit extended discharge times, particularly at a lower current

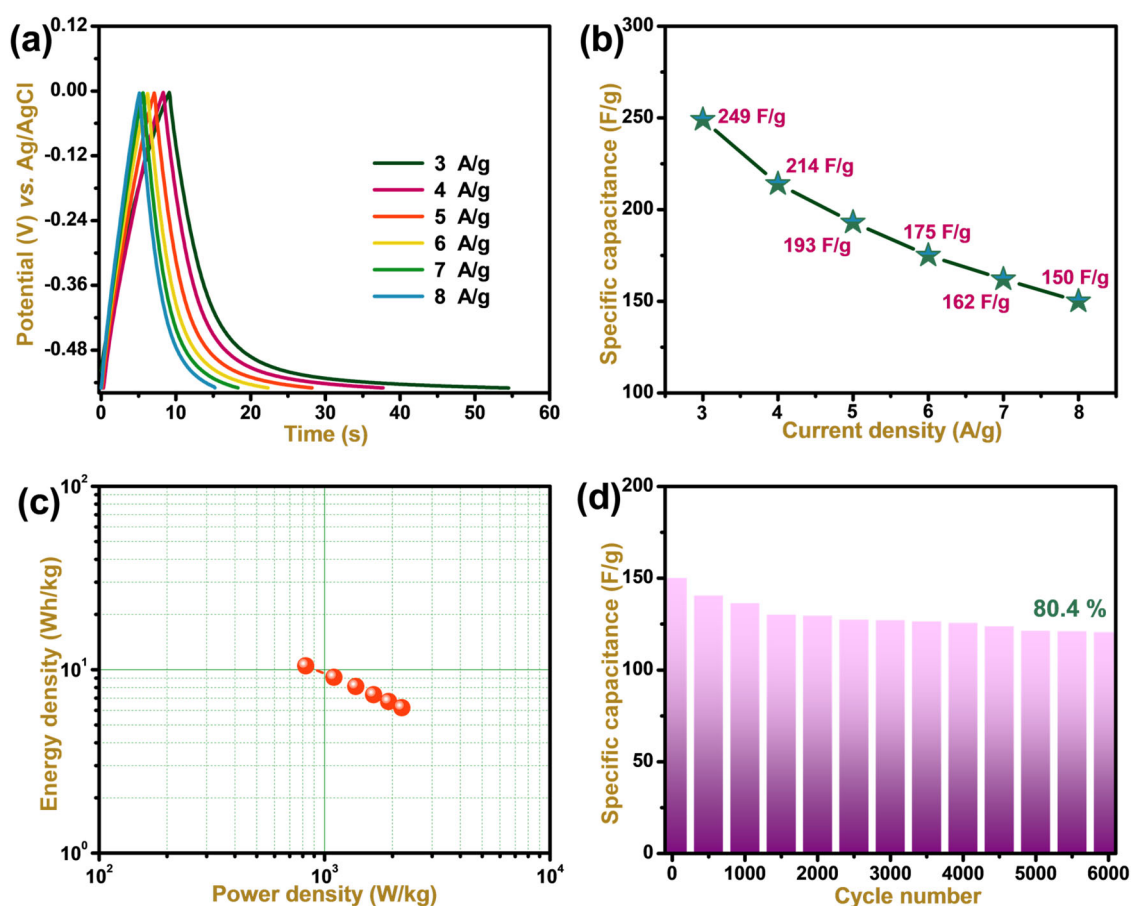


Fig. 4 **a** The GCD plots of Mn_3O_4 electrode at different current density from 3 to 8 A/g respectively, **b** A Cs in F/g derived from GCD data plotted against current density in A/g, **c** Analysis of energy

density in Wh/kg vs power density in W/kg of electrode Mn_3O_4 , **d** A stability plot of Mn_3O_4 electrode at 6000 cycles

density of 3 A/g. This prolonged discharge is due to the efficient utilization of electrochemically active sites and the sustained faradaic redox activity of Mn ions, which enable deeper penetration of electrolyte ions into the porous Mn_3O_4 nanostructure. At lower current density, the slower ion diffusion and charge transfer processes allow more complete electrochemical reactions, thereby resulting in longer discharge duration. Such behavior is typical of pseudocapacitive materials and demonstrates the excellent charge storage capability and high utilization efficiency of the green-synthesized Mn_3O_4 electrode [11, 53–55]. The good reversibility and symmetric nature of the GCD curves at all current densities confirm excellent charge-discharge stability and low internal resistance of the Mn_3O_4 electrode, a result of its intrinsic conductivity and favorable nanostructure.

The Cs values calculated from the GCD curves are plotted against current density in Fig. 4(b). The Mn_3O_4 electrode achieves a high Cs of 249 F/g at 3 A/g, which gradually decreases to 150 F/g at 8 A/g. This decline in capacitance at higher current densities can be attributed to

insufficient time for complete diffusion of electrolyte ions into the porous interior of the electrode material, leading to partial utilization of the active surface area. The electrode maintains over 60% of its initial capacitance at high current, demonstrating excellent rate capability. The enhanced electrochemical behavior can be directly linked to the unique morphology observed in the SEM analysis, which shows a distinct, aggregated, porous, and granular structure of the Mn_3O_4 nanoparticles. This architecture allows for faster ion transport, better electrolyte access, and enhanced surface reactivity, which is crucial for sustaining high capacitance at elevated current densities. The porous framework also reduces diffusion paths and contributes to high power density.

The energy and power density performance of the Mn_3O_4 electrode is evaluated through a Ragone plot, shown in Fig. 4(c). The electrode delivers competitive energy densities while retaining high power densities, making it a promising candidate for high-performance supercapacitor devices. Figure 4(d) presents the cycling stability of the Mn_3O_4 electrode over 6000 continuous cycles at a fixed current

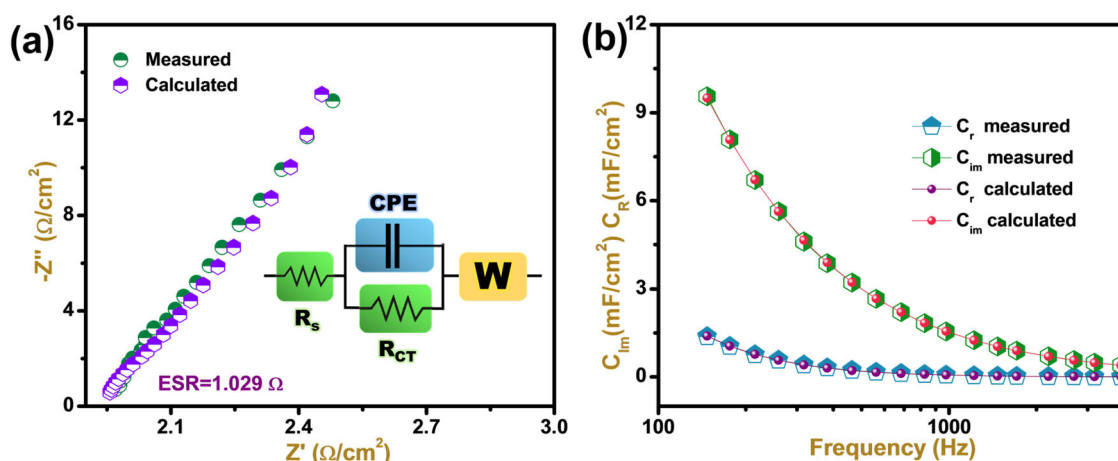


Fig. 5 The Nyquist plot in **a** emphasizes the electrode's electrochemical impedance characteristics (EIS) of Mn_3O_4 electrode, insert fitting circuit, **b** the depict real and imaginary capacitance versus frequency of the Mn_3O_4 electrode

density. The electrode retains approximately 80.4% of its initial capacitance after 6000 cycles, signifying outstanding long-term stability and structural integrity. This impressive cycling stability can again be credited to the porous, granular morphology of Mn_3O_4 nanomaterials, which buffers mechanical stress and maintains consistent electrochemical contact over extended cycling. The structural robustness, provided by the interconnected nanoparticle networks formed via green synthesis with *Cassia tora* leaf extract, contributes significantly to the preservation of capacitance and long-term electrode performance. These results demonstrate that the biosynthesized Mn_3O_4 nanomaterial not only delivers high energy and power densities but also offers superior electrochemical durability, making it highly suitable for practical asymmetric supercapacitor applications.

4.5 EIS analysis

The EIS analysis of the Mn_3O_4 electrode is illustrated in Fig. 5(a), which presents a Nyquist plot fitted with an equivalent circuit (inset) to extract key resistance and capacitance parameters. The semicircular region in the high-frequency domain corresponds to charge transfer resistance (R_{CT}), while the linear tail in the low-frequency region represents Warburg impedance (W), indicating ion diffusion behavior in the electrode. The fitted values reveal a very low solution resistance (R_s) of 1.018 Ω , demonstrating excellent electrolyte conductivity and minimal interfacial resistance at the electrode electrolyte boundary. The charge transfer resistance (R_{CT}) is found to be only 0.3407 Ω , indicating fast faradaic redox kinetics, which is essential for pseudocapacitor electrodes. The constant phase element (CPE), modelled here with a capacitance of 0.0105 F, accounts for the non-ideal capacitive behavior due to surface roughness and porous morphology. The Warburg element

($W = 0.3375$ F) reflects the effective ion diffusion through the porous Mn_3O_4 network, confirming the electrochemical accessibility of the electrode interior. This porous and granular morphology, as observed in SEM, significantly enhances ionic diffusion and contributes to the excellent electrochemical performance observed. A Fig. 5(b) shows the frequency-dependent real (C_r) and imaginary (C_{im}) capacitances of the Mn_3O_4 electrode. The sharp rise in C_r at lower frequencies indicates enhanced capacitive behavior due to improved ion interaction at the interface, while the behavior of C_{im} suggests efficient energy dissipation and ion mobility across the electrode. The overall impedance analysis confirms that the green-synthesized Mn_3O_4 electrode possesses low resistance, high electrochemical activity, and efficient ion transport pathways [56, 57], factors that synergistically enable superior performance. (Note: The concept and analysis of complex capacitance are elaborated in Supporting Information Section S2.3).

5 Solid-state device

The electrochemical behavior of the Mn_3O_4 -based asymmetric solid-state supercapacitor device (ASSD) ($\text{Mn}_3\text{O}_4 \parallel 1\text{M PVA-KOH} \parallel \text{AC}$) was evaluated using CV, as shown in Fig. 6(a). The voltage window (0 to 2.4 V) defines the safe operating range of a supercapacitor, and our device shows a stable window in the tested electrolyte, confirming its efficiency and suitability for an energy storage device [58]. The CV curves, recorded at various scan rates from 5 to 100 mV/s, display a nearly symmetric, quasi-rectangular shape with minor redox humps, confirming the combined capacitive and pseudocapacitive behavior of the device. At lower scan rates (5 and 10 mV/s), the device demonstrates larger integrated area and clear faradaic peaks, which signifies efficient redox charge storage

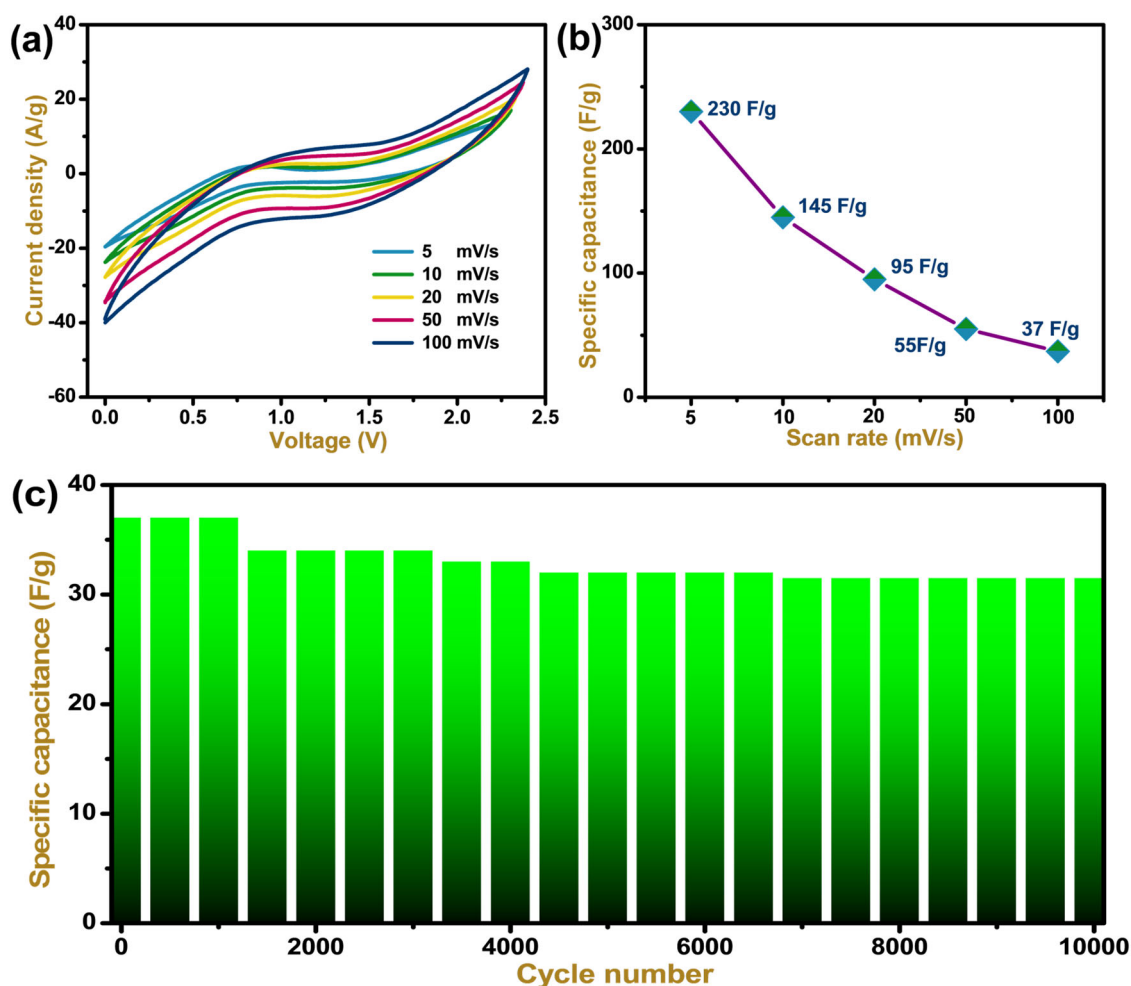


Fig. 6 **a** the CV curves of the $\text{Mn}_3\text{O}_4||1\text{M PVA-KOH}||\text{AC}$ ASSD device recorded at sweep rates ranging from 5 to 100 mV/s, displaying the charge storage potential of the ASSD device, **b** A plot of C_s in F/g

versus scan rate (mV/s), **c** the stability plot of ASSD device, 97.6% capacitance retention after 10,000 cycles

due to the Mn ion transitions at the positive electrode. As the scan rate increases to 100 mV/s, the CV profile maintains its shape without significant distortion, indicating good rate capability, fast ion diffusion, and stable electrochemical kinetics within the solid-state polymer gel electrolyte (PVA-KOH). The synergistic interaction between Mn_3O_4 (as the positive electrode) and activated carbon (as the negative electrode) ensures a wide operating potential window and enhanced energy storage behavior. This well-balanced charge storage, stemming from the redox-active Mn_3O_4 and double-layer contribution of AC, enables efficient operation of the device even at higher sweep rates [59–61]. A Fig. 6(b) shows the variation of C_s with scan rate, where a maximum C_s of 230 F/g is achieved at 5 mV/s, gradually decreasing to 37 F/g at 100 mV/s. This trend is typical for hybrid supercapacitors, where limited ion accessibility at higher scan rates causes partial electrode activation. The decrease from 145 to 37 F/g is a consequence of the finite time

available for ionic movement and redox conversion at elevated scan speeds.

The cycling performance of the solid-state device was assessed by repeated charge-discharge testing over 10,000 cycles, and the results are shown in Fig. 6(c). The device demonstrates exceptional cyclic stability, retaining 97.6% of its original C_s even after prolonged cycling. This outstanding electrochemical durability can be attributed to the robust electrode-electrolyte interface provided by the polymer gel electrolyte (1 M PVA-KOH), which ensures mechanical flexibility, stable ionic conduction/transport, and effectively prevents electrode delamination or degradation [62, 63]. The green synthesized Mn_3O_4 nanoparticles possess a porous and granular morphology (as observed in SEM), offering a large electroactive surface area and mechanical buffering that enable stable faradaic reactions during extended cycling. The strong adhesion between the Mn_3O_4 and the current collector promotes efficient charge transfer and minimizes internal resistance, thereby

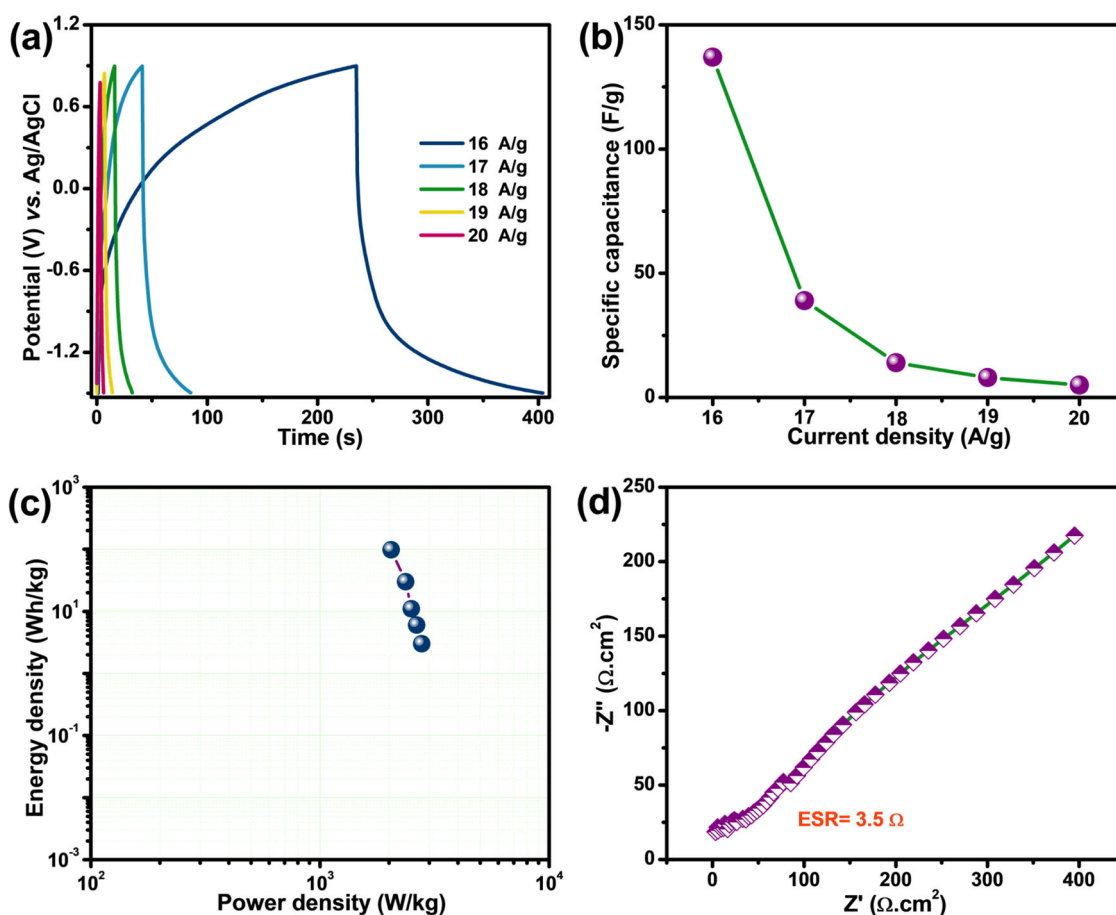


Fig. 7 **a** The GCD curves at varying current densities from 16 to 20 A/g, showcasing the charge-discharge characteristics of the asymmetric solid-state supercapacitor device (ASSD), **b** A graph of $C_{s(GCD)}$ in F/g versus current density (A/g), **c** A plot of energy density (ED) in Wh/kg

against power density (PD) in W/kg, **d** The EIS plot, indicating a low equivalent series resistance (ESR) of 3.5 Ω, reflecting minimal internal resistance and high conductivity within the system

contributing to minimal capacity fading. Collectively, these synergistic effects stable electrode electrolyte interactions, spongy nanostructured morphology, and strong current collector adhesion account for the superior cyclic stability (97.6% retention after 10,000 cycles), positioning this Mn_3O_4 -based solid-state device as a highly promising candidate for next-generation flexible and wearable energy storage applications. Cycle life is vital for the long-term reliability of supercapacitors, as it shows their ability to withstand a repeated number of cycles without major performance loss. Our device exhibits excellent cycling stability with minimal capacitance fading, confirming its promise for durable energy storage device.

The GCD curves of the fabricated asymmetric solid-state supercapacitor device (ASSD) at high current densities ranging from 16 to 20 A/g are shown in Fig. 7(a). The discharge time progressively decreases with increasing current density, indicating a decrease in the utilization of the electroactive material due to limited ion diffusion time. At 16 A/g, the longest discharge profile results in a maximum

Cs of 137 F/g, while at 17, 18, 19, and 20 A/g, the values drop sharply to 39, 14, 8, and 5 F/g, respectively, as shown in Fig. 7(b). This steep decline in capacitance at higher current densities is attributed to insufficient time for complete redox reaction and restricted electrolyte ion access to the inner surface of the porous electrode matrix [46]. The reduced performance at higher loads underscores the importance of ion diffusion dynamics and highlights that the device performs most efficiently at lower current densities. The retention of capacitive behavior at such high current densities still suggests robust charge transport and good interfacial contact within the electrode/electrolyte matrix. The charging and discharging times are crucial for practical supercapacitors, and our device exhibits rapid and stable charge-discharge behavior, confirming its suitability for high-power energy storage.

The insight into asymmetric solid-state supercapacitor device (ASSD) device energy storage capability is provided in Fig. 7(c), which displays a Ragone plot of ED (Wh/kg) versus PD (W/kg). At 16 A/g, the device

Table 2 Comparison of the specific capacitance, energy density, and power density of our synthesized ASSD device with previously reported asymmetric devices

Sr. No.	Asymmetric device electrode		$C_{s(CV)}$ (F/g)	ED (Wh/kg)	PD (W/kg)	Stability in %		Ref.
	Anode	Cathode				Retention	No. of cycles	
1.	polyaniline/ Mn_3O_4	AC	—	33.8	152	58	9000	[78]
2.	Mn_3O_4 @ MB-AC	MB-AC	266.46	119.91	1800.08	99.7	5000	[79]
3.	Mn_3O_4 /CC	AC	94.3 mF/cm ²	25 μ Wh/cm ²	0.64 mW/cm ²	—	—	[80]
4.	Mn_3O_4 / graphene	carbon nano-tube/Graphene	72.6	32.7	22.9 Wh/kg	86	10000	[81]
5.	Mn_3O_4 -GP	AC	132	47	202.5	81.6	5000	[82]
6.	ZnO/CNT	Mn_3O_4 /fCNT	189	1.1	2200	—	10000	[83]
7.	CNT-FeO	CNT-MnO	135.2	37	10.3 kW/kg	100	10000	[84]
8.	Mn_3O_4	graphene	56	124.4	—	82.4	10000	[85]
9.	MnO_2 - Mn_3O_4	AC	74.2	118.3	115329.9 kW/kg	98.6	10000	[86]
10.	Mn_3O_4	AC	—	120	26 kW/kg	80	500	[87]
11.	Mn_3O_4	AC	230	98	2064	97.6	10000	Our work

The bold values indicate the best/maximum performance parameters obtained in this study

$C_{s(CV)}$ = Specific capacitance by cyclic voltammetry plots

ED = Energy density

PD = Power density

achieves a remarkable ED of 98 Wh/kg with a corresponding PD of 2064 W/kg, which reflects the successful integration of high energy and high-power performance. With increasing current density, the ED reduces to 30, 11, 6, and 3 Wh/kg for 17 to 20 A/g, respectively, whereas the PD continues to increase to 2365, 2504, 2643, and 2782 W/kg, showcasing the device potential for rapid energy delivery, the specific capacitance results of our ASSD device are compared with those of previously reported devices in Table 2. This energy power trade-off is a typical feature of pseudocapacitive systems [64]. The PD represents how quickly a supercapacitor can deliver its stored energy, which is essential for real applications such as electric vehicles, backup power, and portable electronics, where rapid energy bursts are required. A higher PD ensures fast charge-discharge capability without performance loss, making it as critical as energy density in practical devices. In this work, our ASSD device exhibits competitive values compared with the energy density (ED) and power density (PD) values of previously reported devices, as summarized in Table 2, while maintaining good energy density and cycling stability, confirming its potential for high-performance energy storage [65, 66]. The Nyquist plot in Fig. 7(d) further confirms the device's electrochemical integrity, revealing a relatively low equivalent series resistance (ESR) of 3.5 Ω . The near-linear slope in the low frequency region reflects good ionic diffusion, while the small semicircle in the high frequency region indicates a low charge transfer resistance, confirming minimal internal resistive losses [67]. These characteristics, combined with the excellent conductivity of the Mn_3O_4

electrode and intimate contact with the PVA-KOH gel electrolyte, contribute to the high performance of the ASSD, making it suitable for high-rate, long-lasting energy storage systems.

6 Conclusions

This study demonstrates a facile, eco-conscious route for synthesizing Mn_3O_4 nanomaterials with *Cassia tora* leaf extract without the use of chemical reducing agents or external additives. The as-prepared Mn_3O_4 nanoparticles showcased a highly granular nanostructure, conducive to enhanced electrochemical activity. Comprehensive structural and morphological characterizations affirmed the crystalline quality and nanoscale dimensions of the synthesized materials. Electrochemical studies in a 1 M KOH electrolyte revealed high specific capacitance, excellent rate capability, and exceptional long-term cycling performance, establishing the effectiveness of the green Mn_3O_4 electrode. The fabricated (Mn_3O_4 ||1M PVA-KOH||AC) ASSD device exhibited impressive energy and power density characteristics, along with robust cycling stability. These outcomes collectively affirm the promise of *Cassia tora*-derived Mn_3O_4 as a sustainable and high-performance electrode material, positioning it as a competitive alternative for future energy storage technologies focused on environmental sustainability and cost effectiveness.

Data availability

Data will be made available as per request.

Supplementary information The online version contains supplementary material available at <https://doi.org/10.1007/s10971-026-07116-0>.

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Compliance with ethical standards

Conflict of interest The authors declare no competing interests.

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