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Synthesis of MnO₂ Nanostructures for Supercapacitor is an Efficient Electrode Material to Improve Energy Storage: Effect of Annealing Temperature

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Abstract

To assess the impact on the physicochemical and electrochemical characteristics of manganese oxide (MnO_2) nanostructures (NSs), a hydrothermal technique was used to synthesize nanostructures, which were then thermally annealed at different temperatures. The successful synthesis of MnO_2 NSs was confirmed by structural and morphological characterization. According to electrochemical characterisation, the pseudocapacitive behaviour of the MnO_2 -based electrode is significantly influenced by the annealing temperature, with 400 °C (MO-1), 500 °C (MO-2), and 600 °C (MO-3) as the respective temperatures. In a 1 M KOH electrolyte, the optimized MO-1 electrode showed a specific capacitance of 280 F/g at 10 mA/g. Additionally, after 5000 GCD cycles, the MO-1 electrode showed outstanding cycling stability, with nearly 98.3% retention of its initial capacitance. An asymmetric supercapacitor (ASSC) device assembled with MO-1 as the positive electrode and activated carbon as the negative electrode delivered a specific capacitance of 126.7 F/g at 10 mA/g and maintained 95.4% of its capacitance over 5000 cycles. The ASSC device also achieved an energy density of 39.6 W h/kg and a power density of 3750 W/kg at 10 mA/g.

Keywords: Manganese oxide (MnO_2), Hydrothermal method, Nanostructures (NSs), Supercapacitor, Energy density

1. Introduction

As global energy demand continues to rise and concerns over climate change and dwindling fossil fuel supplies grow, the need for cleaner, more sustainable energy solutions has become increasingly urgent. Renewable sources like solar, wind, and tidal power are now at the centre of efforts to meet this demand responsibly. In this context, technologies for efficient energy storage and conversion are gaining momentum, particularly electrochemical catalysis and supercapacitors (SCs), which show great promise in helping to manage and balance energy demand [1-4]. SCs, referred to as ultracapacitors, are a type of advanced energy storage device. SCs are especially useful in portable electronics because they can deliver high power, recharge quickly, and last through many charge–discharge cycles. Depending on the charge-storing mechanism, SCs generally fall into three categories: electric double-layer capacitors (EDLCs), pseudocapacitors, and hybrid capacitors [5-6]. EDLCs work by storing energy at the interface between the electrode and the electrolyte through electrostatic forces, a process that doesn't involve chemical reactions. Pseudocapacitors, on the other hand, rely on fast and reversible chemical (Faradaic) reactions, which allow them to store more energy. Hybrid SCs combine both approaches, aiming to balance energy storage capacity and power output, making them suitable for a wide range of practical applications [7-8].

SCs employing metal-oxide semiconductors (MOS) typically exhibit pseudocapacitive behaviour, in which charge storage is governed by Faradaic redox reactions at the electrode–electrolyte interface [9]. The ability of transition metal oxides (TMOs) to undergo reversible changes in oxidation states, along with their environmentally friendly nature and structural tunability, makes them promising candidates for electrode materials in advanced energy storage

systems [10]. Currently, noble metal-based electrodes such as iridium oxide (IrO_2), MOF-based NSs, and ruthenium oxide (RuO_2) are considered among the most efficient for use as SC electrodes. However, their widespread adoption in industrial-scale applications is hindered by the precious scarcity of metals and high cost [11-12]. Consequently, developing efficient SCs derived from earth-abundant elements has become a critical research priority. TMO semiconductors have attracted considerable interest in this context due to their widespread natural availability, low environmental impact, and ability to undergo reversible redox reactions at the surface, making them highly suitable for applications in both energy conversion and storage systems [13]. TMOs, which involve two or more oxidation states, often exhibit enhanced electrochemical properties. The multiple oxidation states can lead to improved charge storage capacity, higher electrochemical activity, and better electronic conductivity. These advantageous characteristics have positioned TMOs as promising candidates for battery-type electrodes in SCs [14].

The advancement of economically viable, highly efficient, and durable materials is crucial for the practical implementation of SCs technologies, which play a significant role in the transition toward sustainable energy systems [15] [16]. To address the limitations and risks associated with the use of RuO_2 , manganese oxide (MnO_2) has emerged as a promising alternative for SCs electrode materials. MnO_2 is particularly attractive due to its multiple oxidation states, moderate electrical conductivity, diverse morphological structures, and favourable electrochemical characteristics, making it suitable for energy storage applications [17]. In addition, MnO_2 NSs have been extensively investigated as a promising electrode material for SCs due to its nearly ideal rectangular cyclic voltammetry profiles, high specific capacitance (C_s), low cost, and environmental compatibility. One of the distinguishing features of MnO_2 NSs is their ability to exist in multiple oxidation states, which significantly influences their structural diversity and

defect-rich morphologies. These characteristics make them particularly suitable for SCs applications. Furthermore, the optimization of manganese by tuning physico-chemical characteristics to form porous oxide offers a pathway to enhance electrochemical performance. Such composite materials exhibit synergistic effects, making them highly attractive for SCs applications [18].

To date, little research has been conducted on MnO₂ for its applicability in SCs applications. Sun et al. [19] synthesized MnO₂ interconnected nanosheets via a CVD route and reported a high C_s of 180 F/g along with high specific energy (E_d) in 1 M Na₂SO₄ electrolyte. Singu et al. [20] used a SILAR method to prepare α -MnO₂ and γ -MnO₂ nanospheres, achieving a C_s of 262 F/g with E_d of 18.3 W h/kg. Similarly, Tang. et al. [21] Fabricated α -MnO₂ nanorods hydrothermally for SC applications and observed a C_s of 152 F/g with 87% retention at a current density of 500 mA/g. In other work, Dhas et al. [22] prepared NiMnO₃ nanostructures using the hydrothermal method and demonstrated a C_s of 435 F/g at 5 mV/s in 1 M KOH, with complete stability over 2,000 cycles. Jing et al. [23] synthesized MnO_x@rGO nanostructures hydrothermally, reporting a C_s of 402 F/g with 90% retention over 10,000 charge–discharge cycles.

The pseudocapacitive potential of MnO₂ is well recognised, but inherent drawbacks, including its modest electrical conductivity and structural instability, hinder its practical use. To address these issues, a variety of tactics have been investigated, such as carbon compositing and nanostructuring. However, properly characterising the physicochemical properties of pristine MnO₂ NSs remains a significant problem that requires a methodical, focused approach. By carefully using thermal annealing as a key technique to maximise the crystallinity, defect chemistry, and ultimately the electrochemical performance of hydrothermally synthesized MnO₂ NSs, this study demonstrates its uniqueness. We explicitly examine annealing as a crucial

performance-determining parameter, in contrast to earlier research that frequently uses it as a subsequent step. Here we rigorously analysing the relation between the charge storage capacity and the annealing temperature, which we show to be a key, direct, and controllable parameter. Our method is validated by the excellent specific capacitance of 280 F/g and the remarkable cycling stability (98.3% retention after 5000 cycles) of optimised MnO₂ electrode, which is annealed at 400 °C. Additionally, this annealing optimisation strategy is demonstrated by the successful fabrication of an asymmetric supercapacitor device (ASSC) that delivers a high energy density of 39.6 W h/kg, marking a substantial leap in the design of high-performance MnO₂-based electrodes.

2. Experimental section:

2.1 Materials and characterization

The commercially available reagents were used to synthesize MnO₂ NSs. These chemical reagents include manganese chloride tetrahydrate (MnCl₂·4H₂O), ammonium heptamolybdate ((NH₄)₆Mo₇O₂₄), Urea (CH₄N₂O), ethylene glycol (C₂H₆O₂), and potassium hydroxide (KOH), which were purchased from Fumes Chemical, Kolhapur, India. The chemicals, such as NF, AC, NMP solvent, and PVDF binder, were purchased from Sigma-Aldrich Co. Ltd. and used without further purification in chemical reactions and in the preparation of the electrode and electrolyte. Fourier transform infrared (FT-IR) spectroscopy was conducted on a Nicolet Nexus 470 spectrometer using pure KBr as the background. Powder XRD patterns were obtained on a Bruker D8-Phaser (Cu-K α radiation, $\lambda=1.5406\text{\AA}$) within the scanning range of 5° - 80°. Sample morphologies were observed by FE-SEM using a Jeol JSM-IT200 spectrometer with an energy dispersive spectrometer (EDS) (EDS Oxford Instruments). X-ray photoelectron spectroscopy (XPS) measurements were recorded on a JEOL ASIA PTE LTD JPS 9030 system with Al K α

radiation ($h\nu = 1486 \text{ eV}$). The surface area of the MnO_2 -based NSs was evaluated through N_2 adsorption-desorption analysis using a Tristar-3000 surface area analyser, applying the Brunauer-Emmett-Teller (BET) method. The pore size distribution and pore volume were derived by analysing the desorption branch of the isotherm utilising the Barrett-Joyner-Halenda (BJH) algorithm.

2.2 Synthesis of MnO_2 NSs:

MnO_2 NSs were synthesized by first preparing a 1 M solution of manganese chloride in 30 mL of DI water, which was stirred for 5 min. While stirring continued, this solution was heated to 80°C for 30 min. The pH was maintained at 8 by the drop-by-drop addition of 1 mL of NH_4OH . Hydrothermal processing was carried out by sealing the precursor solution in a Teflon-lined autoclave and heating it to 130°C for 5 h. After the reaction, the autoclave was cooled to room temperature.



Fig. 1: Schematic representation of the hydrothermal synthesis of MnO₂-NSs at different annealing temperatures from 400 to 600 °C at 3 h.

The solid product was gathered, purified through successive washes with DI water and ethanol, and dried. To analyze how annealing temperature influences the material, the product was annealed at 400, 500, and 600 °C. These samples were labelled MO-1, MO-2, and MO-3 in that order for identification in subsequent analysis. **Fig. 1 provides a schematic overview of the entire synthesis process.**

3. Result and discussion:

The effect of annealing temperature on the formation and structural evolution of MO-1 NSs was investigated using TG study. As shown in Fig. 2(a), the MO-1 NSs exhibited a distinct weight loss of approximately 25.7% over the temperature range of 380 to 430 °C. Based on this observation, an annealing temperature of 450 °C was selected for the thermal decomposition of precursors and formation of the oxide phase. The structural properties of the synthesized MO-1 NSs were further analyzed via XRD, as depicted in **Fig. 2(b)**. The observed diffraction peaks are consistent with the standard data for ICDD card No. 00-044-0141, confirming the formation of a tetragonal MnO₂ NSs phase with space group I4/m [24]. The calculated lattice parameters were $a = b = 9.78 \text{ \AA}$ and $c = 2.86 \text{ \AA}$. The average lattice constant across multiple planes was approximately $10.17 \text{ \AA}$, closely matching the reference values, indicating that the synthesised material is free of internal stress or strain [25]. The XRD patterns exhibit sharp and well-defined peaks corresponding to various crystallographic planes, including (110), (200), (310), (400), (211), (330), (420), (411), (440), (600), (431), (521), (002), and (541), located at 2θ values of 12.78° , 18.1° , 28.84° , 36.69° , 37.52° , 39.01° , 41.22° , 49.86° , 52.85° , 56.37° , 56.92° , 60° , 65.11° , and 69.71° , respectively. At lower annealing temperatures (e.g., 400 °C), the MO-1 NSs displayed broader peaks and reduced

intensity, suggesting lower crystallinity and smaller grain sizes. NSs corresponding to the high-intensity (310) diffraction peak were estimated using the Debye-Scherrer equation [24] :

$$D = \frac{\kappa \lambda}{\beta \cos \theta} \quad (1)$$

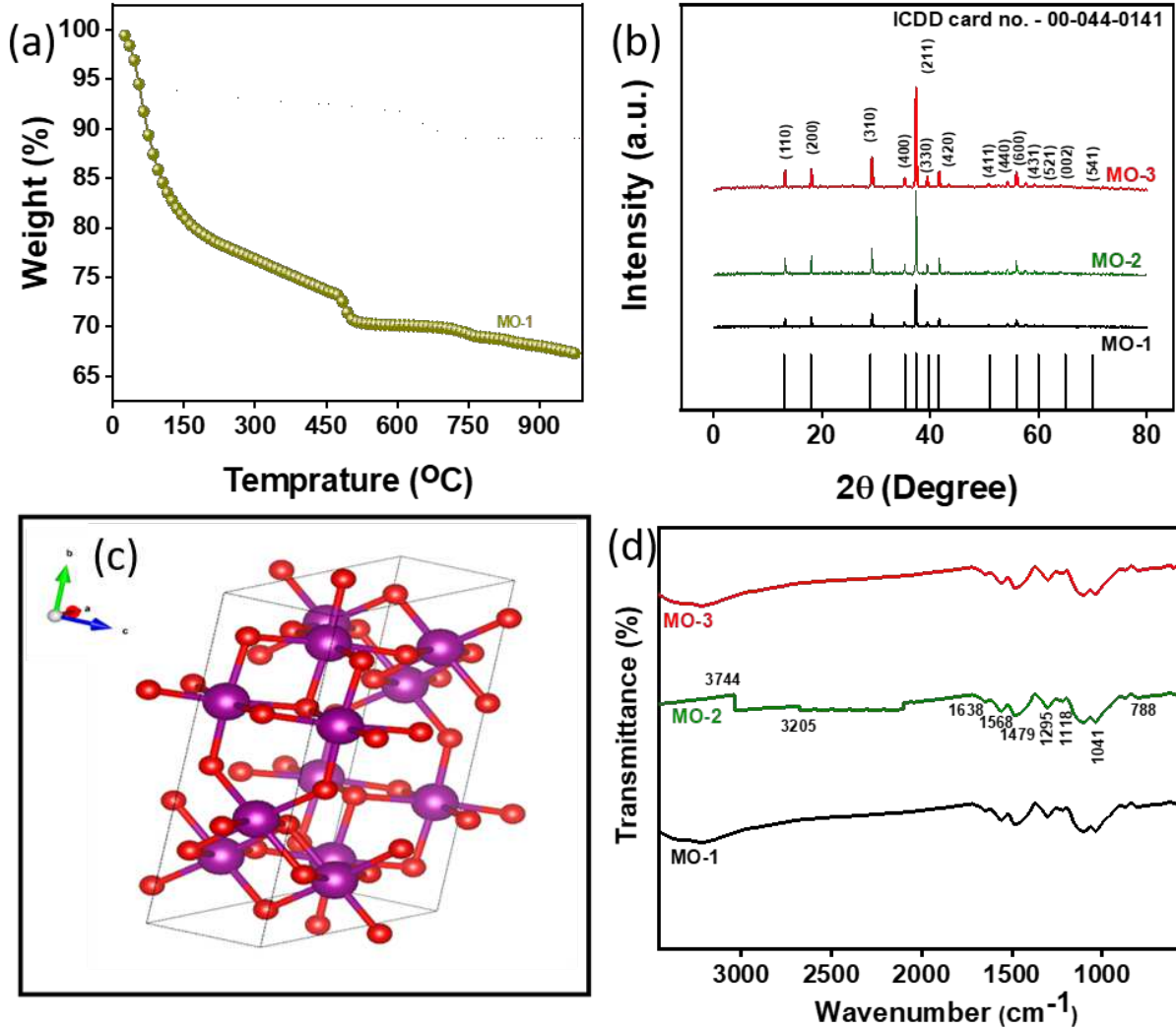


Fig. 2: (a) TG analysis of MO-1 NSs, (b) XRD patterns of MO-1, MO-2, and MO-3 NSs. (c) 3-D crystal structure of MnO₂ NSs (d) FT-IR spectra of MO-1, MO-2, and MO-3 NSs.

As the annealing temperature increased to 500 °C and 600 °C (MO-2 and MO-3), the XRD profiles showed enhanced peak sharpness and intensity, indicating improved crystallinity, grain growth, phase purity, and a reduction in structural defects. Notably, a subtle variation in peak intensity and

broadening was observed near $2\theta = 27.62^\circ$, suggesting minor structural modifications influenced by annealing temperature. The crystallite size (D) of MnO_2 where, D refers to the crystallite size in nm, K is the shape factor (~ 0.9), λ denotes the wavelength of the X-ray radiation (nm), β is the full width at half maximum (FWHM) of the diffraction peak (rad), and θ is the Bragg angle corresponding to the peak position (rad). Based on this equation, the calculated crystallite sizes for the MO-1, MO-2, and MO-3 NSS were 16.3 nm, 18.1 nm, and 21.4 nm, respectively. These results indicate that the crystallite size increases with higher annealing temperatures, as evidenced by reduced peak broadening in the XRD patterns.

The relatively smaller crystallite size at 400°C is likely due to suppressed grain growth and a higher concentration of structural defects formed during lower annealing temperatures [25]. This trend is attributed to thermally driven grain growth at elevated annealing temperatures, such as 600°C , which facilitates the coalescence of smaller crystallites into larger grains. As a result, the crystalline size increases, and the overall structural order improves. This thermal effect enhances atomic mobility, leading to a more well-organised lattice and improved crystallinity of the NSSs [26]. The **Fig. 2(c)** illustrates the 3-D cubic crystal structure of MnO_2 NSSs, highlighting its intricate lattice configuration. Additionally, **Fig. S1** reveals the polyhedral shape of the 3-D MnO_2 NSSs, providing a detailed visualisation of the coordination geometry and spatial arrangement of the Mn and O atoms in the crystal matrix.

FT-IR spectroscopy was employed to investigate the chemical bonding of MO-1, MO-2, and MO-3 NSSs annealed at various temperatures. Spectra were conducted in the range of $400\text{--}4000\text{ cm}^{-1}$, as shown in **Fig. 2(d)**. Characteristic absorption bands associated with Mn-O vibrations typically appear in the region of $400\text{--}800\text{ cm}^{-1}$. FT-IR spectra of samples MO-1, MO-2, and MO-3 revealed multiple prominent peaks at 1639, 1638, 1568, 1479, 1391, 1295, 1118, 1097, and 1041 cm^{-1} .

cm^{-1} , corresponding to various molecular vibrational modes. Broad absorption bands detected at 3205 and 2918 cm^{-1} were attributed to O-H stretching vibrations, likely arising from adsorbed water molecules on the surface. Following calcination, these O-H-related bands significantly reduced, indicating the effective removal of moisture and hydroxyl groups upon thermal treatment. In contrast, the appearance of intense absorption peaks below 827 cm^{-1} confirms the formation of Mn-O bonds, validating the structural integrity of the MnO_2 NSs [27].

A detailed compositional and electronic structure analysis of the MO-1 NSs was performed using XPS, as illustrated in **Fig. 3(a–c)**. **Fig. 3(a)** demonstrates the Survey scan spectrum of MnO_2 . The high-resolution Mn 2p spectrum (**Fig. 3(b)**) displays two distinct spin–orbit doublets, indicative of the coexistence of Mn^{3+} and Mn^{4+} oxidation states in the NSs.

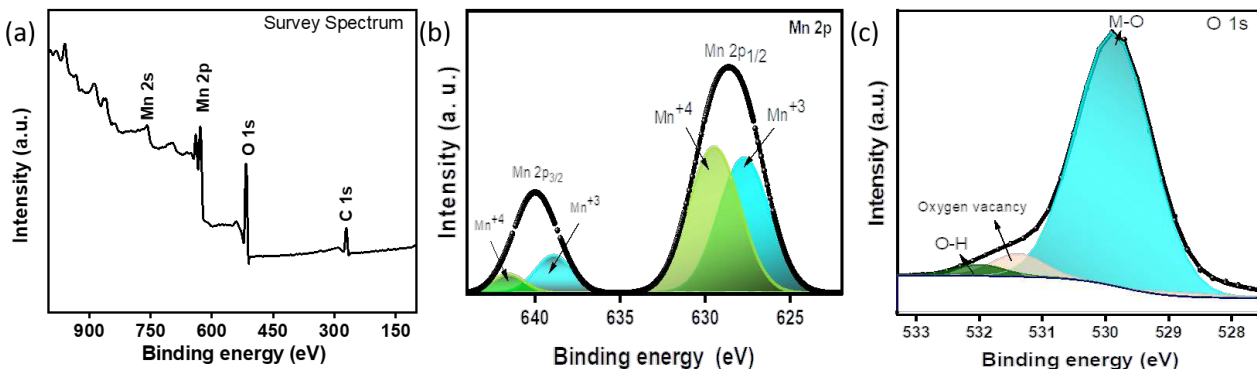


Fig. 3: (a) Survey scan spectrum, Deconvoluted XPS spectrum of (b) Mn, and (c) O elements.

This mixed-valence state suggests the presence of redox-active sites that are beneficial for electrochemical applications. The O 1s spectrum (**Fig. 3(c)**) shows three prominent peaks located at binding energies of 532.1 eV, 531.7 eV, and 529.5 eV. These are assigned to hydroxyl groups from surface-adsorbed water, oxygen species with low coordination numbers, and metal–oxygen bonds, respectively [28]. The spectral deconvolution was carried out using Gaussian fitting, providing insights into the electronic environment and confirming the presence of electrochemically favourable oxidation states.

The surface morphology of the MnO₂ NSs (MO-1, MO-2, and MO-3) is examined using FE-SEM, as illustrated in **Fig. 4(a–c)**. The morphological analysis indicates that the thermal treatment plays a significant role in defining the structural characteristics of the annealed samples. The MnO₂ NSs exhibit irregular, multi-layered polyhedral structures with particle diameters of approximately 700-800 nm. In the MO-1 NSs, smaller crystallite sizes result in a higher specific surface area, which can facilitate enhanced interaction with electrolyte ions and enable more efficient utilization of electrochemically active sites. As the annealing temperature increases from 400 °C to 600 °C, a noticeable growth in particle size is observed. This grain broadening is likely to improve the structural integrity and flexibility of the MnO₂ during repeated GCD cycles, potentially contributing to improved electrochemical performance, including C_s.

At a lower annealing temperature of 400°C, the MO-1 NSs exhibited well-defined growth with uniform distribution, a highly porous architecture, and an interconnected morphology, suggesting that these conditions are favourable for the formation of multi-layered polyhedral structures [29]. The morphological features observed at 400°C align well with the structural information obtained from XRD, which indicates that the MO-1 NSs exhibit moderate crystallinity and an optimal grain size. However, as the annealing temperature increased to 500 °C and 600 °C (MO-2 and MO-3) this porous morphology gradually decreased. The NSs exhibited larger particle sizes and greater nanoparticle agglomeration, resulting in more densely packed structures. This change is attributed to enhanced atomic diffusion and grain growth at elevated temperatures, which contribute to the formation of larger crystallites, as also supported by the XRD data. The aggregation of particles at higher temperatures reduces the accessible surface area, which may negatively impact electrochemical performance [30]. The highly porous, uniformly structured morphology of MO-1 significantly contributes to its enhanced electrochemical performance

compared with other NSs. The increased specific surface area associated with the well-organised NSs promotes efficient ion diffusion and facilitates rapid electron transfer during redox reactions. In comparison, the densely agglomerated morphology observed in MO-3 limits the availability of electrochemically active sites and hinders charge transport, thereby reducing electrochemical efficiency [31]. These findings underscore the critical role of annealing temperature in tailoring the surface morphology and optimizing the electrochemical performance of MnO_2 NSs. The FE-SEM observations are consistent with the XRD results, collectively confirming the structural evolution of the nanostructures as a function of temperature. The multilayered polyhedral morphology observed, particularly in the MO-1 sample, contributes to a higher specific surface area, which is advantageous for SCs applications due to improved charge storage capability. To further investigate the elemental composition, EDS was performed, and the corresponding data are presented in **Fig. 4(d–f)**. EDS analysis of the MO-1 NSs synthesized via the hydrothermal route revealed a manganese atomic percentage of 34.90% and oxygen at 65.10%, aligning with the expected stoichiometry of MnO_2 NSs.

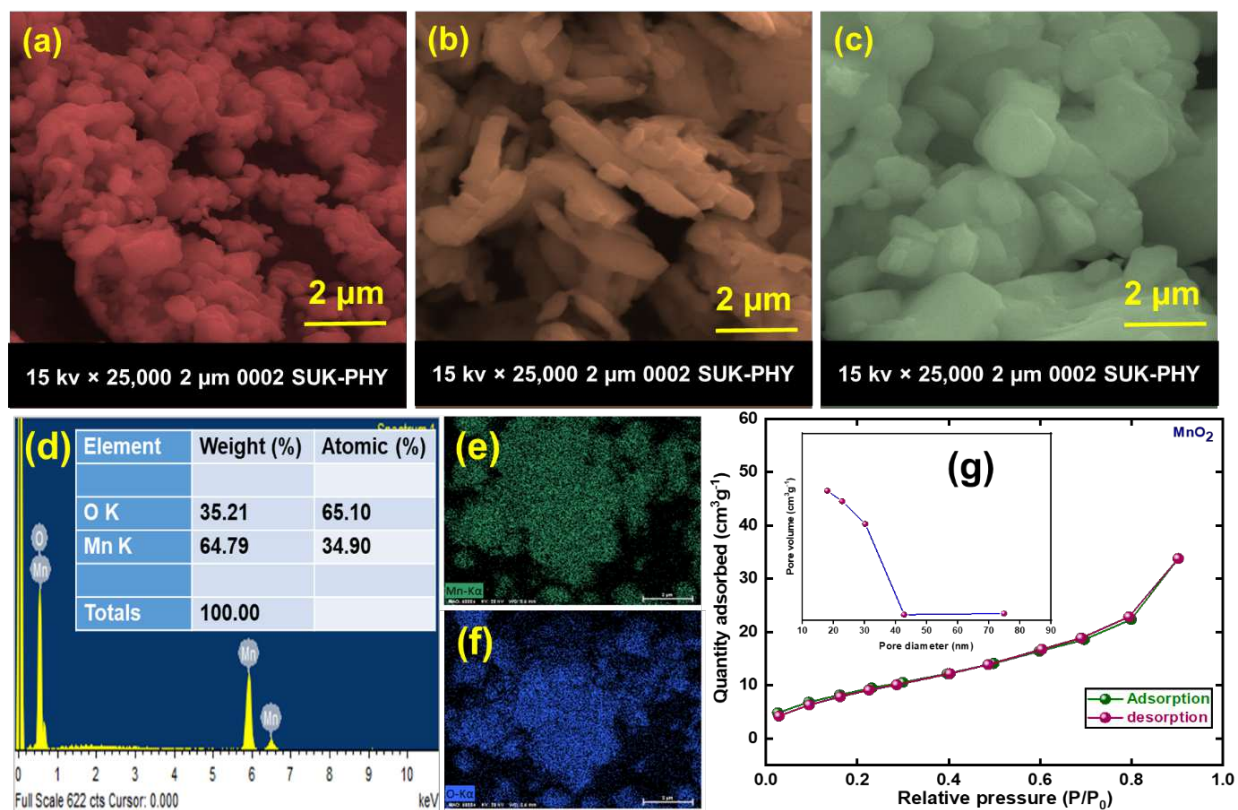


Fig. 4: FE-SEM images of (a) MO-1, (b) MO-2 and (c) MO-3 NSs, (d) EDS spectra of MO-1 NSs and inset atomic weight percentage of corresponding elements, (e-f) elemental mapping of MO-1 NSs for Mn and O elements, respectively. (g) N_2 adsorption-desorption isotherm of MO-1 NSs, inset pore size distribution of MO-1 NSs.

This high oxygen content is consistent with the known oxidation state and chemical structure of the MnO_2 NSs. Given the superior morphological and electrochemical characteristics of the MO-1 NSs, it was selected for detailed elemental analysis. EDS elemental mapping (**Fig. 4e-f**) further demonstrated a homogeneous distribution of Mn and O throughout the sample, with no detectable impurity, confirming the high purity and compositional uniformity of the synthesized MnO_2 NSs. To assess the surface area and porosity of the MO-1 NSs, N_2 adsorption-desorption measurements were conducted using the BET method. The isotherms displayed a type IV pattern

with a characteristic H1 hysteresis loop, as shown in **Fig. 4(g)**, indicating the mesoporous nature of the material. The BET surface area was determined to be 12.48 m²/g. The BJH pore size distribution, presented in the inset of **Fig. 4(g)**, revealed an average pore diameter of approximately 41 nm, further confirming the mesoporous architecture of the synthesized MO-1 NSs.

3.1 Electrochemical analysis:

The electrochemical characteristics of MO-1/NF, MO-2/NF and MO-3/NF electrodes were measured using a three-electrode system (ZIVE Potentiostat, South Korea) in a 1 M KOH electrolyte. The synthesis procedure of the MO-1/NF, MO-2/NF and MO-3/NF electrodes from MO-1, MO-2 and MO-3 NSs is discussed in the supplementary section. The measurements included CV, GCD, and EIS. The prepared MO-1, MO-2, and MO-3 electrodes were used as the working electrodes (WEs), platinum as the counter electrode (CE), and SCE as the reference electrode (RE).

The following formulae were used to calculate the C_s, E_d, and power density (P_d) using the CV and GCD curves [32] [33].

$$C_s \left(\frac{F}{g} \right) = \frac{1}{2\Delta V \times m} \int_{V_1}^{V_2} I(V) dv \quad (2)$$

$$C_s = \frac{I_d \times T_d}{\Delta V \times m} \quad (3)$$

$$E_d \left(\frac{Wh}{kg} \right) = \frac{C_s \times V^2}{2 \times 3.6} \quad (4)$$

$$P_d \left(\frac{W}{kg} \right) = \frac{3600 \times E_d}{T_d} \quad (5)$$

where C_s is the specific capacitance, (ΔV) is the potential window (V), m is the active mass of the electrodes (g), $\int_{V_1}^{V_2} I(V) dv$ is the area under curve (A/cm²), I_d is the discharge current

density (mA/cm^2), T_d is the discharge time (sec), E_d is the energy density, and P_d is the power density.

The electrochemical behaviour of the MO-1, MO-2, and MO-3 electrodes was evaluated by CV over the potential range of 0-0.5 V in 1 M KOH electrolyte at scan rates of 5-100 mV/s. The CV profiles of MO-1, MO-2, and MO-3 are shown in **Fig. 5(a-c)**, respectively. 1 M KOH is used as the electrolyte because of its high ionic conductivity, which enables efficient charge transport and facilitates redox reactions at the electrode-electrolyte interface. A 1 M KOH offers an optimal balance between ionic mobility and electrode material stability. Increasing the concentration beyond this threshold may lead to side reactions or structural degradation of the electrode, while lower concentrations can hinder electrochemical performance by reducing ionic conductivity. In an alkaline solution, the MnO_2 -based electrodes demonstrate pronounced redox activity, primarily due to the reversible redox transitions involving Mn species. The presence of OH^- ions in the KOH electrolyte promotes these Faradaic redox reactions, thereby enhancing C_s . The abundance of OH^- ions also contribute to the high electrocatalytic activity observed in the system. 1 M KOH is a widely adopted electrolyte in SCs. Among the tested electrodes, MO-1 exhibited superior performance in alkaline media, consistent with the efficient redox behaviour of Mn-based oxides. While other electrolytes such as H_2SO_4 , NaOH, and Na_2SO_4 have been explored in related studies [34, 35], KOH remains preferable due to its higher conductivity compared to NaOH. Acidic electrolytes such as H_2SO_4 can compromise the structural integrity of MnO_2 , thereby reducing cycling stability. On the other hand, neutral electrolytes such as Na_2SO_4 , although stable, do not support faradaic redox reactions and thus primarily contribute to electric double-layer capacitance, limiting their overall charge storage capability [36]. The comparative CV curves of

the MO-1, MO-2, and MO-3 electrodes recorded at a scan rate of 100 mV/s are presented in Fig. 5(d).

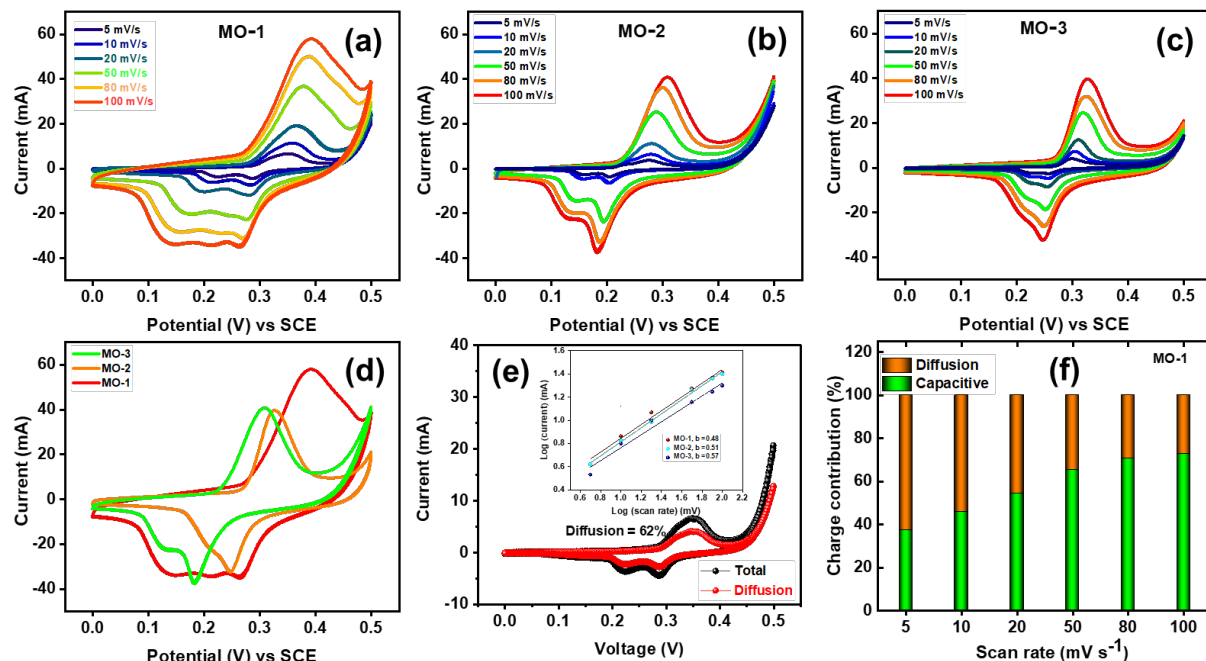


Fig. 5: (a) CV curves of the MO-1 electrode at different scan rates from 5 to 100 mV/s. (b) CV curves of the MO-2 electrode at different scan rates from 5 to 100 mV/s. (c) CV curves of the MO-3 electrode at different scan rates from 5 to 100 mV/s. (d) Comparative CV curves of MO-1, MO-2 and MO-3 electrodes at 100 mV/s scan rate. (e) CV plot of the capacitive and diffusion-controlled contribution of the MO-1 electrode at a scan rate of 5 mV/s, inset (e) plot of log (peak current) versus log (scan rate) of the MO-1, MO-2 and MO-3 electrodes, (f) Bar chart of the charge contribution vs scan rate of the MO-1 electrode at different scan rates from 5-100 mV/s.

Among the other MnO₂ electrodes, the MO-1 electrode exhibits the largest area under the CV curve, indicating superior charge storage capability. A detailed analysis reveals that increasing the annealing temperature initially increases the CV area, with a greater value for the MO-1 electrode. This enhancement is attributed to the improved porosity of the MO-1 NSs, which facilitates greater

electroactive surface area and ion accessibility. However, further increases in annealing temperature beyond MO-1 (i.e., MO-2 and MO-3) result in a reduction in the CV curve. This decline is likely due to particle agglomeration and grain growth at higher temperatures, which reduces the effective surface area and hinders ion transport. The CV curves also display distinct anodic and cathodic redox peaks, confirming the pseudocapacitive behaviour of the MnO_2 NSs, primarily governed by surface or near-surface faradaic redox reactions. Additionally, a slight shift in the anodic and cathodic peak positions is observed, suggesting enhanced ionic and electronic diffusion kinetics during the charge–discharge processes. This behaviour further supports the electrochemical activity and pseudocapacitive nature of the MO-1 electrode, correlating well with its optimized morphology and structural properties [37].

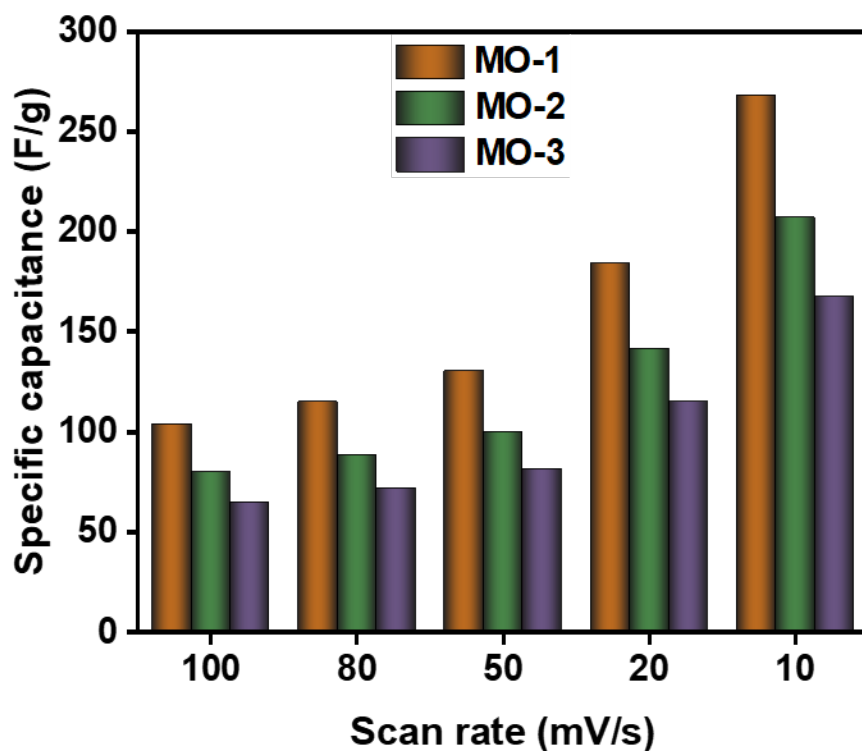


Fig. 6: Bar chart of specific capacitance versus scan rate of MO-1, MO-2, and MO-3 electrodes at various scan rates from 10-100 mV/s.

Among these, the MO-1 electrode demonstrated the highest area under the CV curve at a given current density, which can be attributed to the greater number of electrochemically active sites available for ion intercalation and deintercalation. This enhancement is closely associated with the smaller crystallite size and optimized porous morphology achieved at the corresponding annealing temperature.

In contrast, electrodes annealed at higher temperatures exhibited relatively larger crystallite sizes, which are associated with reduced surface area and fewer accessible active sites for ion transport. As a result, these electrodes exhibited lower electrochemical performance than the MO-1 electrode, highlighting the importance of annealing temperature in tuning structural properties to achieve optimal capacitance [38]. In this study, the MO-1 electrode demonstrated superior supercapacitive performance compared to the other electrodes, as demonstrated by its CV profiles. The C_s of MnO_2 -based electrodes were higher at lower scan rates, which is attributed to the increased time available for electrolyte ions to diffuse and access the electrode material's full surface area. At elevated scan rates, a reduction in capacitance was observed, which can be attributed to factors such as limited electrical conductivity, reduced accessibility of internal pores, and restricted penetration of electrolyte ions, thereby revealing slower ion diffusion. To further elucidate the charge storage mechanism, the kinetic behaviour of the electrodes was analysed using a CV test. A noticeable shift in both anodic and cathodic peaks with increasing scan rate suggests the existence of diffusion-controlled faradaic reactions and surface-controlled capacitive processes. This combination highlights the mixed contributions of pseudocapacitive and double-layer capacitance behaviour in MnO_2 -based electrodes [39]. The analysis of the CV curve (**Fig. 5(e)**) indicates that both diffusion-controlled and capacitive processes contribute to the overall

current response. To quantitatively evaluate these contributions, electrochemical kinetics was examined using the power-law relationship defined by Equation (6) [40].

$$i = av^b \quad (6)$$

Where i and v represent current (mA) and scan rate (mV/s), respectively, and a and b are the adjustable parameters. By applying a logarithmic transformation to both sides of the equation, the b -value, a key parameter for interpreting charge storage behaviour, was determined from the slope of the linear plot of $\log(i)$ versus $\log(v)$. Moreover, the assessment of charge storage contribution is determined through the utilization of the subsequent equation (7) [41]:

$$i = k_1v + k_2\sqrt{v} \quad (7)$$

where k_1 (slope) and k_2 (y-axis intercept of a straight line) are evaluated from the plot of $\frac{i}{\sqrt{v}}$ vs $\sqrt{v}$. The calculated b -values for the MO-1, MO-2, and MO-3 electrodes were 0.48, 0.51, and 0.57, respectively. These values fall within the range of 0.5 to 1.0, suggesting that the charge storage mechanism is governed by a combination of diffusion-controlled faradaic processes and surface-controlled capacitive behaviour. For the MO-1 electrode, the capacitive contribution at a scan rate of 5 mV/s was approximately 38%, as shown in **Fig. 5(e)**. Further analysis of the capacitive and diffusion-controlled charge contributions across a range of scan rates is presented in **Fig. 5(f)**. The results reveal that the capacitive contribution increases progressively with scan rate, indicating faster charge storage at higher scan rates. This behaviour is advantageous for SCs applications, as it suggests enhanced rate capability and efficient energy storage at rapid charge–discharge conditions [42]. The plot of C_s versus scan rate is shown in **Fig. 6**. **Fig. 7(a-c)** illustrates the GCD curves for the MO-1, MO-2, and MO-3 electrodes, measured in 1 M KOH electrolyte at various current densities (10-50 mA/g) within a potential window of 0-0.5 V. The GCD curves display

nearly symmetrical charge and discharge profiles at all current densities, indicating efficient electrochemical reversibility and stability at the electrode–electrolyte interface. The C_s values of the electrodes were calculated using equation 3 based on the discharge curves obtained at different current densities.

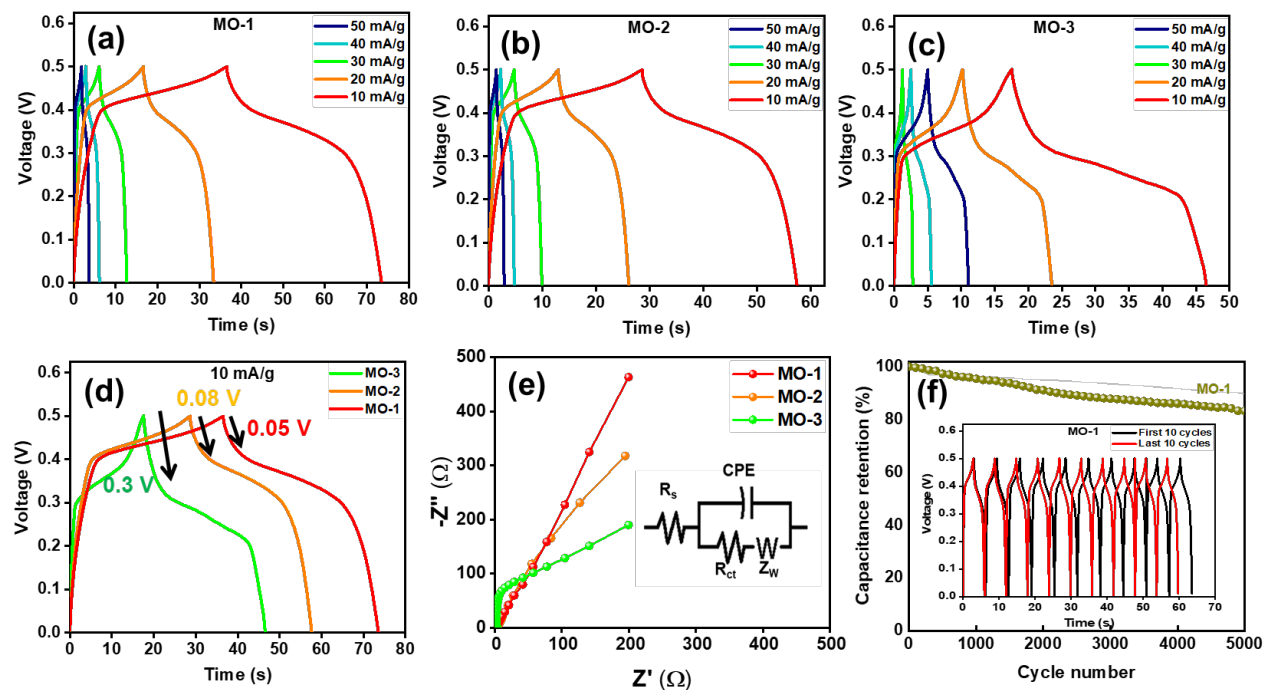


Fig. 7: (a) GCD plot of MO-1 electrode at different scan rates from 10-50 mA/g. (b) GCD plot MO-2 electrode at different scan rates from 10 to 50 mA/g. (c) GCD plot of MO-3 electrode at different scan rates from 10-50 mA/g. (d) Comparative GCD plot of MO-1, MO-2, and MO-3 electrodes at 10-50 mA/g. (e) Comparative EIS plot of MO-1, MO-2, and MO-3 electrodes, inset (e) matched equivalent circuit. (f) Cyclic retention of the MO-1 electrode up to 5000 cycles (inset shows the cyclic retention at 1st and 5000th GCD cycles).

Fig. 7(d) provides a comparative overview of the GCD responses of all three electrodes at 10 mA/g. Among the three electrodes, the MO-1 electrode exhibited the longest discharge time, indicating its superior charge-storage capability. This enhanced performance of the MO-1

electrode is attributed to the abundance of electrochemically active sites, which facilitate improved ion transport and storage. However, a decrease in C_s was observed at higher current densities. This reduction can be attributed to the limited utilization of internal active sites, with the electrochemical reaction predominantly occurring on the outer surface of the electrode due to insufficient ion diffusion into the bulk material under high-rate conditions [43]. The comparative analysis of IR drops as a function of current for MO-1, MO-2, and MO-3 electrodes is presented in **Fig. S2**. Among the three, the MO-1 electrode exhibits the lowest IR drop across, indicating high electrical conductivity and low internal resistance. In contrast, both MO-2 and MO-3 show significantly higher IR drops, suggesting relatively higher charge-transfer resistance and less efficient ion/electron transport pathways. As expected, the IR drop across all electrodes increases with increasing current, as Ohmic losses become more pronounced under high-current conditions. These observations highlight the favourable electrochemical characteristics of the MO-1 electrode, making it a more efficient candidate for high-power SCs. In this study, the MO-1 electrode exhibited the highest C_s of 280 F/g at 10 mA/g, compared with MO-2 (248 F/g) and MO-3 (198.3 F/g). The bar chart of C_s versus current is shown in **Fig. 8**. parameters such as electrode material, morphology, electrolyte used, C_s , cyclic stability, of the MnO_2 -based materials summarized in **Table S1**. To further explore the electrochemical characteristics of the synthesized MnO_2 NSs, EIS was performed. The corresponding Nyquist plot is shown in **Fig. 7(e)**, with the corresponding equivalent circuit shown in the inset. Notably, the absence of a semicircular feature in the high-frequency region suggests minimal charge-transfer resistance (R_{ct}), indicating efficient ion transport and favourable kinetics at the electrode/electrolyte interface [44]. R_{ct} values of the MO-1, MO-2, and MO-3 electrodes are 47.3, 96.1, and 172 Ω , respectively. The comparative EIS spectra for all MO-1, MO-2, and MO-3 electrodes revealed relatively low solution resistance (R_s) values of

0.8, 1.7, and 2.3 Ω , respectively. Among these, the MO-1 electrode exhibited the lowest R_s (0.8 Ω), and R_{ct} (47.3), indicating minimal internal resistance and enhanced electrochemical performance, which is highly favourable for SCs applications.

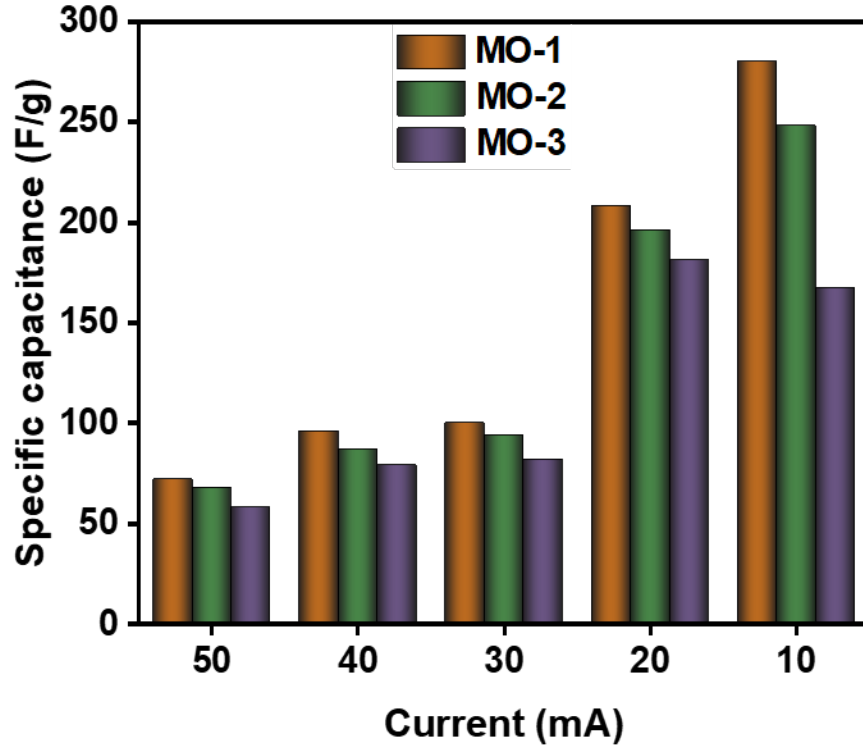


Fig. 8: Bar chart of specific capacitance versus current of MO-1, MO-2, and MO-3 electrodes

Furthermore, the inset in **Fig. 7(e)** shows the equivalent circuit model fitted to the EIS data to extract relevant circuit parameters. **Table 1** revealed EIS parameters of the MO-1, MO-2 and MO-3 electrodes prepared by the hydrothermal method.

Table 1: EIS parameters of the MnO₂-based electrodes prepared by the hydrothermal method

Electrode	R_s (Ω)	R_{ct} (Ω)	Q_1 (mF)	Q_2 (mF)	W (Ω)
MO-1	0.8	47.3	4.5	1.4	0.099
MO-2	1.7	96.1	7.8	4.3	0.17

MO-3	2.3	172	9.1	6.32	0.26
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These findings suggest that optimal annealing temperature is 400 °C (lower), which is essential for achieving superior electrochemical properties. The long-term cycling performance of the MO-1 electrode, optimized at 400 °C, was evaluated using GCD testing over 5000 cycles, as shown in **Fig. 7(f)**. The electrode retained approximately 98.3% of its initial capacitance at a high current density of 50 mA/g, demonstrating excellent electrochemical stability. To further investigate the degradation behaviour of the MO-1 electrode, the first and last 10 GCD cycles are displayed in the inset of **Fig. 7(f)**. The retention of capacitance at high current density reflects a well-conductive network and efficient charge transfer, indicative of robust structural integrity and fast reaction kinetics. Several factors contribute to the high capacitance retention observed, including strong electrode–electrolyte interfacial stability, high electrical conductivity, effective ion transport, and a stable crystalline framework. The multivalent nature of Mn ions plays a significant role in facilitating rapid electron transfer and enhancing redox activity. The nanostructured morphology, particularly in the form of polyhydra-like, contributes to lower resistance by promoting electrolyte penetration and ion diffusion, thereby minimizing resistive losses. Additionally, the chemical stability of electrodes and favourable bonding interactions with the electrolyte help prevent electrode dissolution or significant structural degradation during prolonged cycling. The bar chart of C_s versus current is shown in **Fig. 8**.

3.2 Asymmetric supercapacitor (ASSCs) device:

From a practical perspective, an ASSC's device was assembled, employing MO-1 as the positive electrode and activated carbon as the negative electrode. The fabrication procedure of the ASSC device is discussed in the supplementary section. A schematic representation of the ASSC's

device is provided in **Fig. 9(a)**. To determine the potential window of the ASSCs, separate CV plots of the AC and MO-1 electrodes were recorded at 5 mV/s and are shown in Figure 7(b). The CV curve of the BSH coin cell was recorded at scan rates ranging from 10 to 100 mV/s, as shown in **Fig. S3**, indicating consistent profile shapes across varying scan rates, implying the robust performance of the MO-1//AC ASSCs. Electrochemical measurements were conducted in 1 M KOH + PVA gel electrolyte, including CV and GCD tests, over a range of current densities within a 1.5 V potential window. The corresponding CV and GCD profiles of the fabricated device are displayed in **Fig. 9(b–c)**. Electrochemical performance parameters were derived from the GCD data using equations 5-7. Notably, the maximum C_s attained was 126.7 F/g at a current density of 10 mA/g. The CV response of the MO-1/NF//AC/NF ASSCs indicates that the charge storage mechanism is influenced by both diffusion-controlled and capacitive processes (**Fig. 9(d)**). Furthermore, the electrochemical kinetics were analysed using the relationship described in Equations 6 and 7, thereby allowing quantification of each charge-contribution component. To obtain the device potential, the ions accumulated in both electrodes must be calibrated by modifying the mass loading of the anode and cathode materials. The mass ratio of AC to NiMn₂O₄/C NSs is derived using the formula given [45].

$$\frac{C_+}{C_-} = \frac{C_- \times \Delta E_-}{C_+ \times \Delta E_+} \quad (8)$$

The mass ratio of positive (MO-1) to negative (AC) materials was set to 1:1.

The charge storage kinetics of the MO-1/NF//AC/NF ASSCs device were analysed by plotting the logarithm of the current ($\log(i)$) versus the logarithm of the scan rate ($\log(v)$), as illustrated in **Fig. S4**. Linear fitting of this plot yields the parameter b , which reflects the charge-storage mechanism, as described in Equation 7. The extracted b value for the MO-1//NF//AC/NF ASSCs device is 0.63,

indicating a mixed charge-storage process involving both diffusion-controlled and surface-capacitive behaviours, as the value falls between 0.5 and 1.

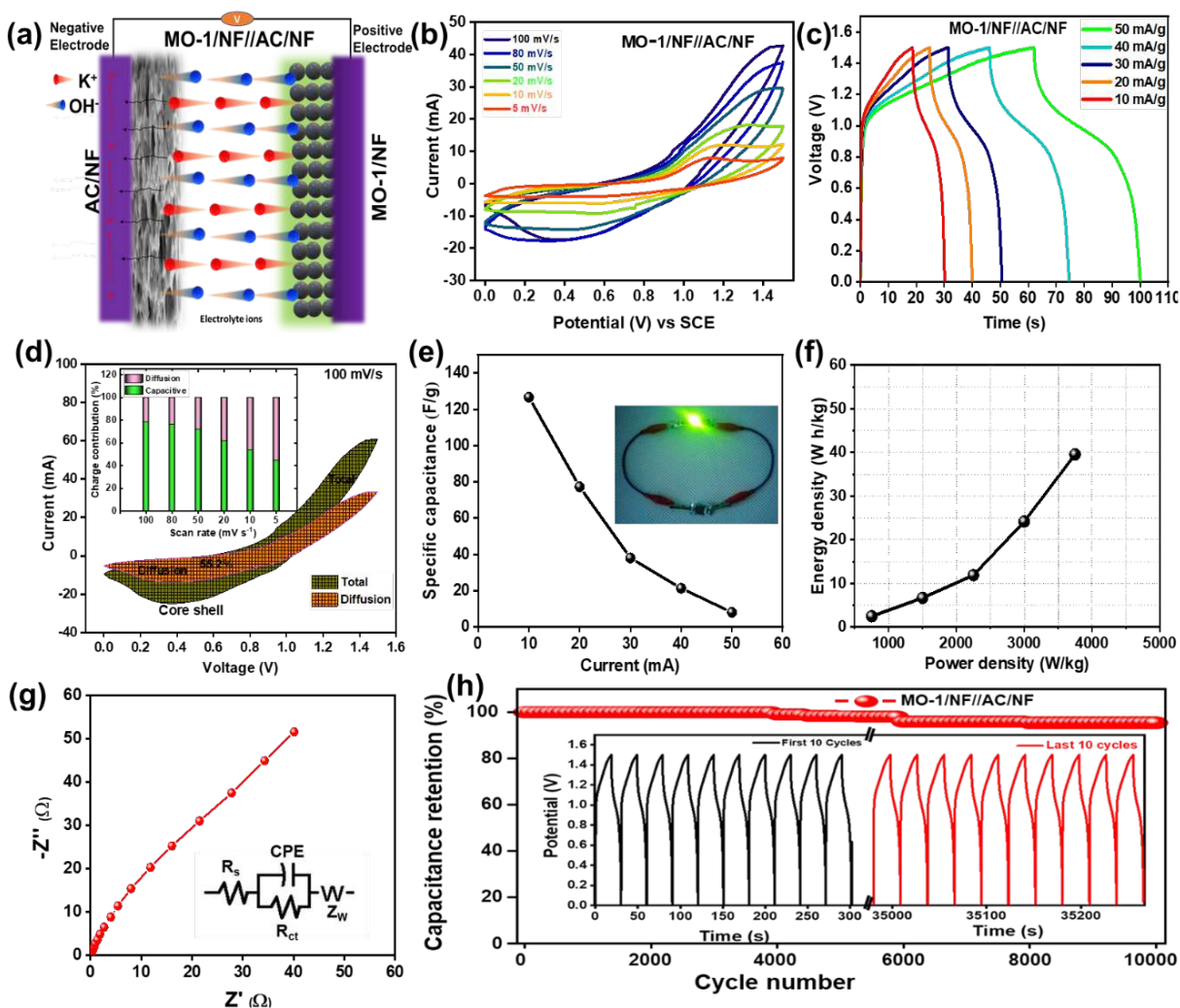


Fig. 9: Asymmetric supercapacitor device of MO-1/NF//AC/NF (a) Schematic representation of ASSCs. (b) CV curves at different scan rates, (c) GCD plot at various current densities, (d) Plot of specific capacitance versus current. (e) Ragone plot (E_d vs power density), (f) EIS curve (h) Cyclic retention up to 10,000 GCD cycles (inset first and last 10 GCD cycles) of the ASSCs.

The analysis of the CV curve (**Fig. 9(d)**) indicates that both diffusion-controlled and capacitive processes contribute to the overall current response of ASSCs. To further distinguish these contributions, the capacitive and diffusion-controlled portions at various scan rates were

quantified and are presented in the bar chart shown in the inset of **Fig. 9(d)**. The data demonstrate that capacitive contributions become more dominant at higher scan rates, consistent with previous findings. **Fig. 9(e)** shows the variation in specific capacitance with scan rate, highlighting the dependence of performance on charge-discharge conditions. Upon charging, MO-1//AC ASSCs demonstrated their efficacy as power supplies by successfully illuminating a red light-emitting diode (LED) for an extended period, as illustrated in the inset of **Fig. 9(e)**. These experimental outcomes and practical demonstrations indicate that the fabricated ASSCs exhibit high energy storage performance. Additionally, the Ragone plot in **Fig. 9(f)** shows that the device delivers an E_d of 39.6 Wh/kg and a P_d of 3750 W/kg at 10 mA/g, as calculated using equations 4 and 5, respectively. **Table 2** provides a detailed comparison of the electrochemical performance of the current MnO₂//AC ASSC configuration and various symmetric and asymmetric configurations using MnO₂ as the electrode material.

Table 2: Detailed comparison of the electrochemical performance between the current MnO₂//AC ASSCs configuration and various other symmetric and asymmetric configurations based on MnO₂ electrode material.

Device Configuration	Electrolyte Used	Specific Capacitance (F/g)	Energy Density (W h/kg)	Power Density (W/kg)	Cyclic Stability (%)/ retention after cycles	Ref
SSCs (AC-MnO ₂ 15%)	1 M Et ₄ NBF ₄	79.43	9.07	85.43	88.88% /1000 cycles	[46]
ASSCs (AC-MnO ₂ 15% // AC)	1 M Et ₄ NBF ₄	98.45	21.07	103.98	91.97% /1000 cycles	[47]
ASSCs (MnO ₂ // Graphene)	1 M Na ₂ SO ₄	37	25.2	100	96% /500	[48]
ASSCs (MnO@C // Co ₃ O ₄)	3 M KOH	166	59.6	1529.8	84.6% / 5000	[20]
ASSCs (PAni/MnO ₂ @CC)	1 M H ₂ SO ₄	1694.25 mF/cm ²	25.58	477.9	77% /1,000	[49]
SSCs MnO ₂ //MnO ₂	1 M Na ₂ SO ₄	119 @1 A/g	59.4	3756	79.8% /2000	[50]

ASSCs MnO ₂ /IL- G//graphene	1 M Na ₂ SO ₄	679	35.2	7.4	89.4% / 10000	[6]
ASSCs MnO ₂ /rEGO//MnO ₂ / rEGO	6 M KOH	226.8	25.5	45	88.8% / 3000	[51]
SSCs Graphene/MnO ₂ // Graphene/MnO ₂	Na ₂ SO ₄ /PV A	759	64.6	15	90.3% / 3000	[52]
fGNS-CNT- MnO ₂ //AC	1 M KOH	202	67	720	95% /1000	[53]
MnO ₂ /NGCF//MnO ₂ / NGCF	1 M Na ₂ SO ₄	133.35	106.7	30.57	100% /12500	[54]
ASSCs MnO ₂ /V ₂ O ₅ /rGO//Mr GO	1 M KCl	-	60.4	90.3	90.3% / 5000	[55]
ASSCs rGO/MnO ₂ @PANI//GF	PVA/KOH gel	120	38.12	28.12	98% / 5000	[56]
ASSCs MnO ₂ //aCNFs	1 M Na ₂ SO ₄	47	16.6	400	97% / 10000	[57]
ASSCs BC@MnO ₂ //AC	1 M Na ₂ SO ₄	209	74.3	1196.4	97.1% / 10000	[58]
ASSCs MO-1//AC	1 M KOH	126.7	36.9	3750	95.4% / 10,000	This Work

EIS was employed to investigate the device's capacitive and resistive characteristics. The corresponding Nyquist plot is presented in **Fig. 9(g)**. Furthermore, the inset in **Fig. 9(g)** shows the equivalent circuit model fitted to the EIS data to extract relevant circuit parameters. In the high-frequency region of the Nyquist plot, the absence of a semicircle indicates a relatively low charge-transfer resistance, thereby facilitating efficient ion transport across the electrode–electrolyte interface. The measured solution resistance of ASSC devices was approximately 2.3 Ω , indicating good electrolyte conductivity. The long-term electrochemical stability of the device was assessed through 5000 GCD cycles, exhibiting a capacitance retention of 95.4%, as depicted in **Fig. 9(h)**. To further investigate the degradation behaviour of ASSCs, the first and last 10 GCD cycles are displayed in the inset of **Fig. 9(h)**. A gradual decline in stability is attributed to the progressive

loss of active electrode materials and activated carbon during cycling. Although the hybrid device utilizes two different electrode materials and operates over a relatively wide potential window, this configuration slightly compromises overall performance compared to individual electrode materials. Nonetheless, the results highlight the promise of MnO₂ NSs as effective components in the development of high-performance hybrid SCs.

4. Conclusion:

In summary, MnO₂ NSs were synthesized via a simple hydrothermal method, followed by different annealing temperatures to evaluate their suitability for SCs applications. Structural and chemical analyses confirmed the successful formation of MnO₂ NSs. XRD confirmed their tetragonal crystalline structure, while FT-IR indicated characteristic Mn–O bond stretching vibrations. FE-SEM revealed a polyhedral morphology, and both EDS and XPS further confirmed the elemental composition and oxidation states. Among the synthesized samples, the MO-1 electrode demonstrated superior electrochemical performance, delivering a C_s of 280 F/g at 10 mA/g in 1 M KOH. It also exhibited excellent cycling stability, maintaining 98.3% of its capacitance after 5000 GCD cycles. Additionally, an ASSC's device achieved an energy density of 39.6 W h/kg and a power density of 3750 W/kg, with 95.4% retention over 10,000 cycles. These results indicate that MnO₂ NSs, synthesized via a controlled hydrothermal process and annealing, have significant potential as electrode materials for high-performance energy storage devices.

Credit authorship contribution statement

Suprimkumar D. Dhas: Writing - original draft, Writing-Review & Editing, Conceptualization, Supervision. **Pragati N. Thonge:** Data curation, Investigation, Methodology. **Aqsa Ghazal:** Validation, Software. **Aravind H. Patil:** Visualisation, Software, Conceptualisation. **Teja M.**

Patil: Formal analysis, Conceptualisation. **Tushar T. Bhosale:** Investigation, Formal analysis. **D. Karthigaimuthu:** Software, **Saifan M. Shaikh:** Conceptualisation, Formal analysis. **Falah Awwad:** Funding acquisition, Project administration, Supervision.

Data availability declarations

Data included in the article/supplementary material is referenced in the article.

Declaration of generative AI in scientific writing

We declare that we haven't used any generative AI tools in the preparation, review, or editing of this work's content.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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