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Effect of Concentration on the Charge Storage Kinetics of Nanostructured MnO₂ Thin-Film Supercapacitors Synthesized by the Hydrothermal Method

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Abstract: In this study, amorphous manganese oxide (MnO₂) nanostructured thin films were synthesized by a simple hydrothermal method. It is well known that the nanostructure plays a crucial role in energy storage applications. Herein, MnO₂ nanostructures ranging from plates to flakes were synthesized without the use of any hard or soft templates. The 4+ oxidation state of Mn was confirmed by X-ray photoelectron spectroscopy. The MnO₂ nanoflake structure has a specific surface area of 46 m²g^{−1}, which provides it with an excellent rate capability and an exactly rectangular cyclic voltammogram (CV) curve. The MnO₂ nanoflake electrode has a high specific capacitance of about 433 Fg^{−1}, an energy density of 60 Whkg^{−1} at 0.5 mAcm^{−2}, and an excellent cyclic stability of 95% over 1000 CV cycles in 1 M aq. Na₂SO₄. Kinetics analysis of the charge storage in the nanoflake MnO₂ sample shows a 55.6% diffusion-controlled contribution and 44.4% capacitive-controlled contribution to the total current calculated at a scan rate of 100 mVs^{−1} from the CV curve.

Keywords: MnO₂ nanoflakes; hydrothermal; charge storage kinetic analysis; specific surface area; supercapacitive performance

1. Introduction

The use of fossil fuels has posed significant problems to modern society, such as increasing fuel costs, pollution, and global warming [1]. These issues can be resolved by developing renewable energy sources and storage technologies [2]. The automobile industry (automobile vehicles) has the largest contribution to environmental pollution. A new variety of vehicles based on electric energy can reduce these problems. The currently available energy storage devices are batteries and capacitors, that exhibit low power density and energy density, respectively. However, modern electronic applications require both the power and the energy density simultaneously, which can be fulfilled by supercapacitors, that also fill the gap between capacitors and batteries [3].

Supercapacitors have high power density, long cycle life, fast charging rate, wide operating temperature range, and enhanced safety and efficiency [4,5]. Supercapacitors are used as auxiliary power sources in electric vehicles, which have a significant potential development in the vehicle

industry [6]. Supercapacitors have a lower energy density compared to batteries. Therefore, research has focused on the enhancement of the energy density parameter of supercapacitors, by developing various type of nanostructured materials using different methods to synthesize composite and surfactant-mediated metal oxides [7,8]. Supercapacitors can be classified into two types, based on their charge storage mechanism and electrode materials. The first type is the electric double-layer capacitor (EDLC), which is based on non-faradic charge storage mechanisms in carbonized electrode materials [9]. The carbon-based materials have high conductivity and large specific surface areas (SSAs), but their theoretical capacitance is limited to a few hundred Faradays in aqueous and organic electrolytes [10,11]. The second type is the pseudocapacitor, in which charge storage occurs via fast redox (faradic) reactions. Conducting polymers (CPs) and metal oxides (MOs) are used as electrode materials in pseudocapacitors [12]. CP electrodes have high electric conductivity, electroactivity, and reversibility (the ability to change the oxidation-reduction state by applying an external electric field) [13]. Cyclic voltammetry (CV) measurements of CPs exhibit peaks at the redox potential. However, the peaks are sensitive to the temperature [14]. The hybrid supercapacitor, which is made up of one EDLC and other pseudocapacitor electrode material, has both types of charge storage mechanism.

MOs undergo a series of redox reactions to exhibit almost rectangular CV shapes, which contribute to high theoretical capacitance—in the order of thousands of Faradays [13–15]. In pseudocapacitors, various transition metal oxides such as RuO_2 [16], IrO_2 [17,18], NiO [19], CoO_x [20], SnO_2 [21], and MnO_2 [22,23] are used as electrode materials. RuO_2 is the ideal and most explored electrode material for supercapacitor applications. It exhibits highly reversible redox reactions, a wide potential window, good thermal stability, high proton conductivity, long cycle life, high rate capability, and metallic-type conductivity. It has the highest specific capacitance (approximately 1000 Fg^{-1}) among pseudocapacitive materials [16,24]. However, the high cost and toxicity of RuO_2 limits its commercial use [24].

MnO_2 has been considered as an alternative electrode material to RuO_2 owing to its low cost, abundant availability, environmental safety, and large theoretical capacitance ($\sim 1300 \text{ Fg}^{-1}$) [25,26]. The various methods used for the synthesis of MnO_2 include the sol-gel [27], dip-coating [28], liquid co-precipitation, electrodeposition [29], spray-pyrolysis [30], and hydrothermal methods [31]. In this study, we used a hydrothermal method for synthesizing MnO_2 thin films. The method is beneficial for the development of nanostructures such as nanoflakes, nano-urchins, nanorods, and nanobelts. The shapes and sizes of the nanostructures can be tuned by changing the hydrothermal synthesis parameters, such as the temperature and time.

This article focuses on the synthesis of MnO_2 thin films by a simple and cost-effective hydrothermal method. MnO_2 nanostructures and their respective SSAs can be tailored by varying the concentration of the Mn precursor. The effect of the nanostructures on the structural, morphological, and surface properties and electrochemical measurements are discussed in detail. The separation of the diffusion and capacitive-controlled current contribution in the total current is also discussed.

2. Experimental Details

2.1. Reagents and Materials

Stainless steel (SS) substrates were used as the current collector for MnO_2 thin film deposition. Potassium permanganate (KMnO_4) and AR grade sodium sulfate (Na_2SO_4) with 99% purity were purchased from SD Fine Pvt. Ltd., Mumbai, India. Hydrochloric acid (HCl) and ethanol were purchased from SD Fine Pvt. Ltd., India and used to clean the substrates. The chemicals required for the synthesis of thin films were used as received without further purification. Double-distilled water (DDW) was used for solution preparation.

2.2. Synthesis of MnO_2 Thin Films

Binder-free MnO_2 thin films were synthesized directly on the SS substrate by a simple hydrothermal method at low temperature. A typical procedure includes 1 mM concentration of KMnO_4 as the Mn

precursor dissolved in 30 mL DDW with constant stirring for 20 min to form a solution. The substrate treatment is crucial in the preparation of thin films. The SS substrates were cleaned with detergent to remove dust particles and grease. The SS substrates were then mirror-polished with zero-grade polish paper, followed by treatments with ethanol and HCl. These SS substrates were inclined against the wall of a beaker and immersed in the KMnO_4 solution. The beaker with the KMnO_4 solution and SS substrates was autoclaved at 90 °C for 2 h. Black thin films were observed on the SS substrates after cooling down autoclave to room temperature. These deposited thin films were rinsed with DDW to remove loosely bound particles and dried at room temperature. These films were denoted as HM1.

The same procedure was repeated for 2, 3, and 4 mM concentrations of Mn precursors, and the resulting thin films were denoted as HM2, HM3, and HM4, respectively. The same hydrothermal parameters as described above (the deposition time and temperature) were used for all the thin films.

2.3. Characterization of the Prepared Samples

The photoluminescence (PL) spectrofluorometer (Fluoromax4, Horiba Ltd., Japan) was used to record PL emission spectra of the material. The structural study of materials was conducted on X-ray diffraction (XRD) spectroscopy, D2 phaser, Bruker AXS Analytical Instruments Pvt. Ltd., Karlsruhe, Germany. X-ray photoelectron spectroscopy (XPS) measurements were carried out on K-alpha, and Thermo Scientific, UK. Surface morphology of the materials were observed at 10 kV potential by field emission scanning electron microscopy (FE-SEM) S-4800 HITACHI, Ltd., Tokyo, Japan. Surface area of the nanostructured material were studied by the Brunauer–Emmett–Teller (BET) method on Quantachrome NOVA 1000e, Austria. The electrochemical measurements, were carried out in a three-electrode system on potentiostat PGSTAT302N Metrohm autolab, Netherlands. The deposited weight of the active material was determined by the weight difference method, i.e., the difference in the weight of substrate before and after deposition.

3. Results and Discussion

3.1. X-ray Diffraction (XRD)

Figure 1a shows the XRD patterns of the MnO_2 thin films synthesized by the hydrothermal method with different concentrations of Mn precursor for diffracting angles 2θ varying between 20° to 80°. The observed XRD peaks at 43.5, 44.48, 50.7 and 74.6° marked with Δ were attributed to the SS substrate. No extra peaks besides the SS peaks were observed, indicating that the prepared thin film materials were X-ray amorphous. The amorphous nature may be due to the low synthesis temperature, which resulted in the presence of water molecules in the material. The material was further characterized by XPS to obtain information about its chemical state.

Figure 1. (a) XRD and (b) photoluminescence spectra of hydrothermally deposited MnO_2 at various precursor concentrations from 1 to 4 mM.

3.2. Photoluminescence (PL)

The PL spectra of all the MnO₂ samples in the range of 375 to 525 nm were recorded at room temperature at 374 nm excitation wavelength using a Xe lamp source. The results are shown in Figure 1b. The PL emission spectra are located within the blue-violet spectral region. The hydrothermally deposited MnO₂ samples exhibit three peaks at 412, 435, and 462 nm, indicating strong blue emission. The bandgaps of the samples can be calculated from the PL wavelengths using

$$E_g = \frac{h \times c}{\lambda}, \quad (1)$$

where, h is the Planck constant; c is the velocity of light, and λ is the wavelength of the absorption peak.

The bandgap of MnO₂ was calculated to be 3.0 eV for the wavelength of 412 nm from the PL spectra. Along with the violet band-edge transition, the violet and blue emissions observed at 435 and 462 nm may be ascribed to oxygen vacancies and dangling bonds on the surface (or surface defects) of the material respectively [32].

3.3. X-ray Photoelectron Spectroscopy (XPS)

XPS studies were performed to investigate the chemical states of the MnO₂ thin film (HM3 sample). The survey scan spectrum in Figure 2a shows the presence of Mn, O, and C elements. The Mn 2p core-level spectra shown in Figure 2b exhibit two major peaks at the binding energies of 653.7 and 642.1 eV corresponding to Mn 2p_{1/2} and Mn 2p_{3/2}, respectively. The spin energy separation of 11.6 eV in Mn2p confirms the presence of Mn in the +4 oxidation state [33–36]. The oxidation state of Mn in MnO₂ can be confirmed from the Mn 3s core level spectra (89.1 and 84.0 eV). The Mn 3s doublet spectra has spin energy separation of 4.9 eV for the MnO₂ structures (Figure 2c), indicating that Mn is present in the +4 charge state. Figure 2d shows the O1s core level spectra of MnO₂. The peaks at 532.5 eV and 529.7 eV were attributed to the presence of H-O-H (water molecule) and Mn-O-Mn bonds, respectively [37–39]. These results indicate that Mn in the hydrothermally synthesized MnO₂ has an oxidation state of Mn (IV). Along with the Mn and O peaks, the high-resolution C1s peak in the survey scan spectrum (Figure 2a) was further studied in detail. The results in Figure 2e show that the peak centered at the binding energy of 284.7 eV results from the sp² (C-C) bond. The other two observed peaks at the binding energies of 286.2 and 287.9 eV are derivatives of carbon in the C-O group and carbonyl or carboxylic groups (C=O), respectively [40].

Moreover, based on XPS spectra, the peak area of Mn⁴⁺ and Mn³⁺ for Mn2p core level spectra mentioned in Table 1, and the ratio of Mn⁴⁺/Mn³⁺ for HM3 sample is 0.77 which ascribed presence of high content of Mn⁴⁺ [41–43].

Table 1. The XPS data of Mn2p for HM3 sample; and corresponding peak areas and Mn⁴⁺/Mn³⁺ values.

Sample Code	Species	Peak Position (eV)	Peak Area	Mn ⁴⁺ /Mn ³⁺
HM3	2p _{3/2} Mn ³⁺	642.1	134113.1	0.77
	2p _{3/2} Mn ⁴⁺	644.6	68664.4	
	2p _{1/2} Mn ³⁺	653.7	38083.0	
	2p _{1/2} Mn ⁴⁺	653.8	64231.1

Figure 2. Typical X-ray photoelectron spectroscopy of HM3 sample: (a) survey, (b) Mn2p, (c) Mn3s, and (d) O1s spectra (e) C1s spectra.

3.4. Field Emission Scanning Electron Microscopy (FESEM)

The surface morphologies of the hydrothermally grown MnO₂ thin films were observed by FESEM. Figure 3 shows the FESEM images recorded at 100 k magnification and an applied potential of 15 kV. At a low concentration of the Mn precursor (HM1), nanoplates of size 200–300 nm were observed. At higher Mn precursor concentrations (HM1 to HM3), the nanostructures converted from nanoplates to nanoflakes. Well-developed and uniformly distributed nanoflakes of size 10–20 nm were observed in the HM3 sample (3 mM concentration of Mn precursor). Such nanoflakes with highly porous structures provide a high SSA. When the concentration of the Mn precursor was increased to 4 mM, the agglomeration of nanoflakes formed, reduces the SSA.

Figure 3. Field emission scanning electron micrograph of samples: (a) HM1, (b) HM2, (c) HM3, and (d) HM4 at 100 k magnification and 15 kV applied potential.

3.5. Growth Mechanism of MnO_2 Thin Films

The growth mechanism of the MnO_2 thin films is shown schematically in Figure 4. After dissolving KMnO_4 of 1 mM concentration in DDW, the K^+ (aq.) and MnO_4^- (aq.) ions were separated with pink color solution. As the concentration of KMnO_4 increased from 1 mM to 4 mM, the color of the solution changed from pink to dark bluish-pink due to presence of more K^+ and MnO_4^- ions. The reaction mechanism is given below [44],

Figure 4. Schematic representation of MnO_2 thin films hydrothermally grown using various concentrations of Mn precursor.

During the reaction in hydrothermal, the MnO_2 nanoparticles started to self-assemble to minimize the energy of the system. At the lower KMnO_4 concentration (1 mM), the Van-der Waals forces and hydrogen bonds between the molecules resulted the formation of MnO_2 nanoplates. As the KMnO_4 concentration increases, more Mn particles participated in the reaction to minimize the energy of the system, and the synthesized nanostructures were altered by the Ostwald ripening mechanism during the hydrothermal reaction [45]. The agglomeration of MnO_2 nanoparticles observed after increasing concentration of the KMnO_4 because more MnO_4^- ions are in contact with each other. Hence, the optimization of the exact concentration of the metal precursor (availability of metal ions) plays a vital role in the nanostructure formation. The availability of the exact number of metal ions with respective energies of the system can assist to develop uniform nanostructures.

3.6. Surface Adsorption De-Adsorption

To study the influence of the Mn precursor concentration on the surface area and porosity of the MnO_2 nanostructured materials, the BET gas adsorption method was employed. The N_2 adsorption-desorption isotherms and corresponding Barrett–Joyner–Halenda pore size distribution (inset graph) of the prepared MnO_2 nanostructured samples are shown in Figure 5a–d. The isotherms of all the MnO_2 samples observed in Figure 5a–d usually correspond to the Type-III category, and the H3 hysteresis loop is mesoporous, according the International Union of Pure and Applied Chemistry (IUPAC) classification criteria [46,47].

Figure 5. N_2 adsorption-desorption isotherms of (a) HM1, (b) HM2, (c) HM3, and (d) HM4. Inset: pore size distribution curves.

The measured SSA and average pore radius (APR) are summarized in Table 2. HM1, which has a nanoplate morphology, has the minimum SSA with a large average pore radius. As the concentration of the Mn precursor increases from 1 to 3 mM, the SSA increases and APR decreases. As the concentration of the Mn precursor is further increased to 4 mM, the SSA decreases because of the agglomeration of the nanoflakes, which was confirmed by FESEM. The largest SSA of $46 \text{ m}^2 \text{g}^{-1}$ with 6 nm APR is observed in the well-developed and uniformly distributed flake-like nanostructures of the HM3 sample. The variations of the SSA and APR are required for intercalation-deintercalation of electrolyte ions in the porous material, which in turn affects the suitability of the material for supercapacitor applications.

Table 2. Sample codes, specific surface area, average pore radius, specific capacitance, energy density and power density of hydrothermally grown all MnO₂ electrodes.

Sample Code	Specific Surface Area (m ² ·g ^{−1})	Average Pore Size (nm)	Weight of Active Material (mg)	Specific Capacitance (Fg ^{−1})	Energy Density (Whkg ^{−1})	Power Density (Wkg ^{−1})
HM1	17	13	0.10	315	43	2.5
HM2	43	8	0.25	392	54	1.0
HM3	46	6	0.29	433	60	0.8
HM4	35	7	0.29	316	43	0.8

3.7. Electrochemical Measurements

The supercapacitive behavior of the MnO₂ nanostructured thin films was characterized by cyclic voltammetry (CV), galvanostatic charge–discharge (GCD), electrochemical impedance spectroscopy (EIS), and cyclic stability measurements. A three-electrode system with platinum as the counter electrode, MnO₂ as the working electrode (1 × 1 cm² deposited area), and saturated calomel (SC) as the reference electrode was used for the electrochemical measurements.

3.7.1. Cyclic Voltammetry (CV)

Figure 6a shows typical CV curves recorded at various concentrations of Mn precursor (HM1 to HM4). The CV curves of all the nanostructured MnO₂ samples were measured in 1 M aqueous Na₂SO₄ electrolyte at a 20 mV s^{−1} scan rate in a 0–1.0 V potential window. The MnO₂ samples (HM1 to HM4) have almost rectangular CV curves indicating ideal capacitive behavior with fast redox reactions [48]. The CV curves shift towards higher current densities as the concentration of Mn precursor increases from HM1 to HM3 and decreases as the concentration is further increased in the HM4 sample.

Figure 6. (a) Cyclic voltammograms of HM1, HM2, HM3, and HM4 at 20 mV/s scan rate; (b) cyclic voltammograms of HM3 at different scan rates (20 to 100 mVs^{−1}); (c) galvanostatic charge–discharge (GCD) curves of HM1, HM2, HM3, and HM4 at 0.5 mAcm^{−2} current density; (d) GCD curves of HM3 at different current densities (0.5 to 2 mAcm^{−2}) in 0–1.0 V potential window in 1 M aq. Na₂SO₄ electrolyte.

There are two types of capacitive charge storage mechanisms in MnO₂ electrodes [28]. The first type is the intercalation of alkali metal ions such as Na⁺ ions during reduction in the MnO₂ electrode and de-intercalation during oxidation [49]. A possible reaction mechanism is:

The second type of capacitive charge storage mechanism involves a surface process in which adsorption/de-adsorption of alkali metal Na⁺ ions occurs on the surface of the MnO₂ nanostructures [50,51]. The reaction mechanism is given by:

The intercalation/de-intercalation process is predominant in crystalline MnO₂ and the surface adsorption/desorption process predominant in amorphous MnO₂ [52]. In the latter case, the capacitive charge storage is due to the surface adsorption/de-adsorption process; therefore, the specific capacitance mainly depends on the SSA of the material. The redox mechanism is mainly governed by the adsorption and de-adsorption of Na⁺ (or H⁺) from the electrolyte onto the surface of the porous nanostructured MnO₂ matrix.

To obtain more information on the electrochemical behavior, the HM3 electrode was characterized at different sweep rates from 20 to 100 mVs^{−1}. This information will lead to a better understanding of the actual participation of the MnO₂ electrode in the redox process [53]. The results are shown in Figure 6b. It can be seen that the current density curves shift towards higher current densities in the HM3 electrode as the scan rate increases. Zhang et al. [54] reported the occurrence of distortions in the CV curves when the scan rate increased. However, in our study, rectangular-like CV curves were consistently observed as the scanning rate increased from 20 to 100 mVs^{−1}. The absence of redox peaks in all the CV curves suggests that the electrode was charged/discharged at a pseudo-constant rate over the complete CV cycle [55].

3.7.2. Galvanostatic Charge–Discharge (GCD)

To calculate the specific capacitance (C_{sp}), energy density (ED), and power density (PD) of the hydrothermally grown MnO₂ nanostructured electrode, galvanostatic charge–discharge versus SCE measurements were carried out in 1 M aqueous Na₂SO₄ electrolyte for 0–1.0 V potential at different current densities. Figure 6c shows the GCD graphs of MnO₂ in HM1 to HM4 samples at 0.5 mAcm^{−2} current density. The GCD graphs of all the MnO₂ samples (HM1 to HM4) show a linear variation in the potential and symmetric charge/discharge curves, which indicates ideal capacitive performance [56]. C_{sp} , ED, and PD were calculated from the GCD curves using the following equations:

$$C_{sp} = \frac{I_d T_d}{m dV}, \quad (5)$$

$$E = \frac{1}{2} C_{sp} V^2, \quad (6)$$

$$P = \frac{E}{T_d}, \quad (7)$$

where I_d is the constant discharge current; T_d the discharge time, m the deposited weight of active material; dV the cycling potential window; V the potential during the discharge cycle; C_{sp} the specific capacitance; E the energy density, and P the power density of the materials.

The specific capacitances calculated from Equation (5) for HM1 to HM4 at the constant current density of 0.5 mAcm^{−2} are listed in Table 2. HM3 shows the longest maximum discharge time and consequently the highest C_{sp} of about 433 Fg^{−1}. Moreover, HM3 has an ED of approximately 60 Whkg^{−1}

and PD of approximately 833 Wkg^{-1} . The specific capacitance varies between 315 to 433 Fg^{-1} in the HM1 to HM4 electrodes.

Subramanian et al. [31] reported similar results by varying the hydrothermal dwelling time from 1 to 18 h and achieved the maximum specific capacitance of about 160 Fg^{-1} . Toupin et al. [57] examined the effect of the annealing temperature on the specific capacitance and obtained the maximum specific capacitance of 180 Fg^{-1} at 2 mVs^{-1} for as-prepared MnO_2 samples. Increasing the annealing temperature increased the decomposition of MnO_2 into Mn_2O_3 and decreased the specific capacitance. Subramanian et al. [53] studied the effect of the Na_2SO_4 electrolyte concentration on the MnO_2 thin film and observed that there was only a small variation in the capacitance. This small difference resulted from the presence of carbon, which has a finite contribution to the double-layer capacitance. Xiao et al. [58] reported the specific capacitance of approximately 220 Fg^{-1} in $\alpha\text{-MnO}_2$ nanotubes prepared by a chemical precipitation method. $\alpha\text{-MnO}_2$ nanorods synthesized via the chemical precipitation method were reported to have a specific capacitance 166.2 Fg^{-1} by Li et al. [59].

The increase in the capacitance with the Mn precursor concentration is due to the change in the nanostructures from nanoplates to nanoflakes. The pores between the nanoflakes can facilitate the penetration of electrolyte ions into the inner region of the nanoflake electrode while the large surface area provides more active sites for electrochemical reactions.

To further investigate the rate capability of the MnO_2 nanostructured electrodes, the GCD curves were measured at various current densities. Figure 6d shows the GCD curves of the HM3 electrode at the current densities of 0.5, 1, and 2 mAcm^{-2} in the 0–1.0 V potential window. The GCD profiles are highly linear and symmetrical, demonstrating that the nanoflake-structure MnO_3 electrode has excellent reversibility and charge–discharge properties. The calculated specific capacitance for the HM3 electrode, which has nanostructured flakes, at different current densities are provided in Table 3. HM3 shows a high specific capacitance as well as a better rate capability even at the high current densities of 1 and 2 mAcm^{-2} (5 and 10 Ag^{-1}). The HM3 electrode shows specific capacitances of 396 and 366 Fg^{-1} with 91% and 84% capacitance retention as the current density increases from 1 to 2 mAcm^{-2} . It is well known that the capacitance decreases with increasing current density because the surface of the electrode is inaccessible at higher current densities [60,61].

Table 3. Specific capacitance, energy density and power density of M3 sample at different current densities.

Sample Code	Current Density (mAcm^{-2})	Specific Capacitance (Fg^{-1})	Energy Density (Whkg^{-1})	Power Density (Wkg^{-1})
HM3	0.5	433	60	0.8
HM3	1	396	55	1.6
HM3	2	366	50	3.3

The above results for the MnO_2 electrode at high current density are much better than the specific capacitances of about 150 and 122 Fg^{-1} at 5 and 10 Ag^{-1} current densities, respectively, reported previously for nanosheet MnO_2 by Kundu et al. [62]. Zhao et al. [63] reported specific capacitances of about 221 and 176 Fg^{-1} at 0.5 and 1 mAg^{-1} , respectively. A mesoporous MnO_2 nanowire array exhibited specific capacitances of 493 and 84 Fg^{-1} at current densities of 4 and 12 Ag^{-1} , respectively [64]. The variation of the specific capacitance with the current density in a $\text{MnO}_2/\text{C}/\text{TiO}_2$ shell/core array electrode was studied. The specific capacitance was found to be 539.2 Fg^{-1} at 2 Ag^{-1} , 280.9 Fg^{-1} at 10 Ag^{-1} , and 223.7 Fg^{-1} at 20 Ag^{-1} , respectively [65].

The high rate capability in the HM3 sample is attributed to its nanoflake-like structure which results in a shorter ion diffusion path and increased electronic conductivity.

3.7.3. Stability

A supercapacitor requires not only high capacitance but also cycling stability, which is one of the critical parameters limiting its applicability. The cycling stability of the HM3 sample was investigated at room temperature over up to 1000 continuous CV cycles at a scan rate of 100 mVs^{-1} in $1 \text{ M Na}_2\text{SO}_4$ aqueous electrolyte. The results are shown in Figure 7a.

Figure 7. (a) Capacitance retention (in percentage) with respect to cycle number in HM3. (b) Nyquist plots of the HM1, HM2, HM3 and HM4 electrodes at 10 mV potential in $1 \text{ M Na}_2\text{SO}_4$ electrolyte. The inset graph shows the magnified Nyquist plot.

The nanoflake MnO_2 (HM3) electrode shows a high capacitance retention of about 95%. The capacitance decreases stepwise after 100 cycles. The capacitance loss may be due to the dissolution of Mn ions into the aqueous electrolyte [66,67]. A MnO_2 -based device reported in the literature showed a capacitance retention of 80% after 1000 GCD cycles [68]. Ke et al. reported a capacitance retention of 93% after 1000 cycles for a hollow nest-like nanostructured MnO_2 thin film [69]. The mixed nanorods and nanoplates in $\alpha\text{-MnO}_2$ electrode showed 83% capacitance retention after 100 cycles at 200 mA.g^{-1} current density [53].

3.7.4. Electrochemical Impedance Spectroscopy (EIS)

EIS was used to investigate the resistive and capacitive behavior of the thin films due to the electrochemical intercalation occurring at the interface between the electrode and electrolyte. The EIS was performed using the three-electrode system described earlier in $1 \text{ M Na}_2\text{SO}_4$ aqueous electrolyte over a frequency range from 0.1 Hz to 10 kHz at 10 mV potential. In general, the Nyquist plot for a supercapacitor consists of three parts, namely, a series resistance at the high-frequency region indicated by the intercept to the Z' axis (real impedance). It is a contact resistance between electrolyte and electrode surface. A semicircle at the mid-frequency region which represents the charge transfer reaction at the interface between the electrode and the electrolyte [70], and a straight line representing the Warburg resistance at the low-frequency region due to ion diffusion into the electrode material [71–73].

Figure 7b shows the Nyquist plots for all the MnO_2 nanostructured samples (HM1 to HM4). The Nyquist plots for all the samples do not exhibit semicircles at the mid-frequency region. The absence of the semicircular regions implies the possibility of electrochemical reactions according to Equation (3). The EIS data were fitted with the help of ZSimpWin based on the equivalent electrical circuit. The obtained series resistances, capacitance and Warburg resistance for MnO_2 (HM1, HM2, HM3 and HM4) samples are mentioned in Table 4. The HM3 sample shows a smaller series resistance (R_s) compared to other samples. All the MnO_2 samples show a short arc and a 45° diagonal line with respect to the real impedance (Z') axis, indicating capacitive behavior [74,75].

Table 4. Values of series resistance, capacitance, and Warburg resistance of MnO₂ obtained by Zsimwin fit.

Sample Code	Series Resistance (Ω)	Capacitance (F)	Warburg (ΩS^{-1})
HM1	1.32	0.024	0.048
HM2	1.28	0.084	0.143
HM3	1.04	0.115	0.149
HM4	1.41	0.072	0.096

3.7.5. Storage Kinetics Studies Using CV plot

To study the detailed charge storage behavior of the MnO₂ samples, we analyzed the kinetics based on the CV measurements. In general, the relationship between the current (i) and scan rate (ϑ) is given by:

$$i = a\vartheta^b, \quad (8)$$

where i is the current at specific voltages; ϑ is the scan rate; a and b are constants. The total current exhibited by the material includes contributions from (1) the surface-controlled capacitive process (ion adsorption/desorption) and (2) diffusion-controlled charge storage (fast faradic reaction of redox species). A value of $b = 1$ in Equation (8) indicates capacitive-dominant behavior, whereas $b = 0.5$ represents a diffusion-controlled process [76,77].

From Figure 8a, $b = 0.64$, which means that the HM3 sample exhibits both capacitive and diffusion-controlled behavior [78]. The capacitive effect was investigated by measuring how the current changed with respect to the scan rate at a specific potential. The b values of HM3 for the cathodic and anodic curves at 0 to 1.0 V vs the SCE potential are shown in Figure 8d. The values of b at different potentials in the cathodic and anodic scans range between 0.5 to 1 and show both diffusion and capacitive-controlled behavior.

The specific contribution of the capacitive and diffusion-controlled mechanisms to the total current can be quantified using:

$$i(v) = K_1\vartheta + K_2\vartheta^{1/2}, \quad (9)$$

where $i(V)$ is the current response at a specific voltage; ϑ is the scan rate; $K_1\vartheta$ the capacitive current, and $K_2\vartheta^{1/2}$ the diffusion-controlled current. K_1 and K_2 are determined by plotting $i(V)/\vartheta^{1/2}$ vs $\vartheta^{1/2}$ to separate out the charges from the capacitive and diffusion-controlled processes [78]. Figure 8b shows a CV plot of the capacitive contribution (highlighted area) to the total charge storage for the HM3 sample at 100 mVs^{−1} scan rate in 1 M aq. Na₂SO₄. It was observed that about 97%, 88%, 48%, and 94% of the charge storage contribution in the HM1, HM2, HM3, and HM4 samples, respectively, are due to the capacitive process. Here, we show the capacitive and diffusion-controlled contributions in the HM3 sample under different scan rates from 20 to 100 mVs^{−1} in Figure 8c, and also in the HM1, HM2, and HM4 samples under different scan rates from 20 to 100 mVs^{−1} in Figure S1.

It seems that the capacitive process is unaffected by the scan rate whereas the diffusion-controlled contribution decreases with increasing scan rate for all the MnO₂ samples. The redox intercalation contribution decreases with increasing scan rate because there is insufficient time for ion diffusion into the lattice at a high scan rate. The capacitive and diffusion-controlled contributions of all the MnO₂ samples at different scan rates are listed in Table S1. The high specific capacitance obtained for the HM3 sample compared to the other samples (HM1, HM2, and HM4) is attributed to the larger contribution from the diffusion-controlled process in HM3, which agrees with the GCD results described earlier.

Figure 8. (a) The peak current plotted against the scan rate to determine the b value of the HM3 anodic curve. (b) Capacitive contribution of total charge storage at a sweep rate of 100 mVs⁻¹ for the HM3 sample. Comparison of capacitive (shaded area) and diffusion-controlled contribution in HM3 sample at 100 mVs⁻¹ scan rate. (c) Capacitive and diffusion contributions to the total charge storage at different scan rates (20–100 mVs⁻¹) in the HM3 sample.

In addition to the comprehensive comparison of the electrochemical behavior of the hydrothermally deposited MnO₂ thin films, a radar chart is shown in Figure 9. Each vertex of the chart corresponds to a supercapacitive parameter, and the integral area under the curve implies the electrochemical performance of the samples. From Figure 9, it can be seen that the integral area of the HM3 sample is notably larger compared to the other samples. This confirms that the HM3 sample with a nanoflake structure exhibits a large SSA, a large potential window, a small minimum series resistance, and a large diffusion-controlled contribution, which contribute to its high specific capacitance.

Figure 9. Comparison of MnO₂ sample performance based on six supercapacitive parameters.

4. Conclusions

We successfully synthesized nanostructured MnO₂ thin films directly on SS substrate via the hydrothermal method. The concentration variation of the KMnO₄-tailored morphology of MnO₂ from plates to flakes is due to the rearrangement of the nanoparticles with the increase in the number of Mn ions. A 3 mM concentration of KMnO₄ produced a nanoflake morphology with a high SSA, resulting in the maximum specific capacitance. From the charge storage kinetics, we can conclude that the diffusion-controlled current is dominant at low scan rates while the capacitive-controlled current is dominant at higher scan rates. The diffusion-controlled current is highest in the nanoflake sample because of its high porosity and electrical conductivity, which increase the contact time between the material and electrolyte. All these aspects of the nanoflake sample allow it to exhibit an acceptable level of supercapacitive performance. The performance of hydrothermally deposited MnO₂ thin films was compared based on the six supercapacitor parameters.

Supplementary Materials: The following are available online at <http://www.mdpi.com/1996-1073/13/22/6124/s1>, Figure S1: Charge storage kinetics of hydrothermal deposited MnO₂ sample. Table S1: Capacitive and diffusion controlled contribution of hydrothermally deposited all MnO₂ thin films at various scan rate (20–100 mVs^{−1}) in 1 M Na₂SO₄ aq. Electrolyte.

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References

1. Zhang, F.; Xiao, F.; Dong, Z.H.; Shi, W. Synthesis of polypyrrole wrapped graphene hydrogels composites as supercapacitor electrodes. *Electrochim. Acta* **2013**, *114*, 125–132.
2. Ng, K.C.; Zhang, S.; Peng, C.; Chen, G.Z. Individual and Bipolarly Stacked Asymmetrical Aqueous Supercapacitors of CNTs/SnO₂ and CNTs/MnO₂ Nanocomposites. *J. Electrochem. Soc.* **2009**, *156*, A846–A853.
3. Conway, B.E. *Electrochemical Supercapacitors Scientific Fundamentals and Technological Applications*; Kluwer Academic/Plenum Publisher: Dordrecht, The Netherlands, 1999.
4. Yiğit, D.; Güngör, T.; Güllü, M. Poly(thieno[3,4-b][1,4]dioxine) and poly([1,4]dioxino[2,3-c]pyrrole) derivatives: P- and n-dopable redox-active electrode materials for solid state supercapacitor applications. *Org. Electron. Phys. Mater. Appl.* **2013**, *14*, 3249–3259.
5. Wu, C.H.; Hung, Y.H.; Hong, C.W. On-line supercapacitor dynamic models for energy conversion and management. *Energy Convers. Manag.* **2012**, *53*, 337–345.
6. Vural, B.; Boynuegri, A.R.; Nakir, I.; Erdinc, O.; Balikci, A.; Uzunoglu, M.; Gorgun, H.; Dusmez, S. Fuel cell and ultra-capacitor hybridization: A prototype test bench based analysis of different energy management strategies for vehicular applications. *Int. J. Hydrogen Energy* **2010**, *35*, 11161–11171.
7. Wei, W.; Cui, X.; Chen, W.; Ivey, D.G. Manganese oxide-based materials as electrochemical supercapacitor electrodes. *Chem. Soc. Rev.* **2011**, *40*, 1697–1721.
8. Desai, B.D.; Fernandes, J.B.; Dalal, V.N.K. Manganese dioxide—A review of a battery chemical Part II. Solid state and electrochemical properties of manganese dioxides. *J. Power Sources* **1985**, *16*, 1–43.
9. Simon, P.; Burke, A. Nanostructured carbons: Double-layer capacitance and more. *Electrochem. Soc. Interface* **2008**, *17*, 38–43.
10. Jurewicz, K.; Vix-Guterl, C.; Frackowiak, E.; Saadallah, S.; Reda, M.; Parmentier, J.; Patarin, J.; Béguin, F. Capacitance properties of ordered porous carbon materials prepared by a templating procedure. *J. Phys. Chem. Solids* **2004**, *65*, 287–293.
11. Fernández, J.A.; Morishita, T.; Toyoda, M.; Inagaki, M.; Stoeckli, F.; Centeno, T.A. Performance of mesoporous carbons derived from poly(vinyl alcohol) in electrochemical capacitors. *J. Power Sources* **2008**, *175*, 675–679.

12. Sharma, P.; Bhatti, T.S. A review on electrochemical double-layer capacitors. *Energy Convers. Manag.* **2010**, *51*, 2901–2912.
13. Arbizzani, C.; Mastragostino, M.; Meneghello, L. Polymer-based redox supercapacitors: A comparative study. *Electrochim. Acta* **1996**, *41*, 21–26.
14. Patil, D.S.; Pawar, S.A.; Patil, P.S.; Kim, J.H.; Shin, J.C. Silver nanoparticles incorporated PEDOT-PSS electrodes for electrochemical supercapacitor. *J. Nanosci. Nanotechnol.* **2016**, *16*, 10625–10629.
15. Mastragostino, M.; Arbizzani, C.; Soavi, F. Polymer-based supercapacitors. *J. Power Sources* **2001**, *97–98*, 812–815.
16. Sakiyama, K.; Onishi, S.; Ishihara, K.; Orita, K.; Kajiyama, T.; Hosoda, N.; Hara, T. Deposition and properties of reactively sputtered ruthenium dioxide films. *J. Electrochem. Soc.* **1993**, *140*, 834–839.
17. Audichon, T.; Napporn, T.W.; Canaff, C.; Morais, C.; Comminges, C.; Kokoh, K.B. IrO₂ Coated on RuO₂ as Efficient and Stable Electroactive Nanocatalysts for Electrochemical Water Splitting. *J. Phys. Chem. C* **2016**, *120*, 2562–2573.
18. Chen, Y.M.; Cai, J.H.; Huang, Y.S.; Lee, K.Y.; Tsai, D.S. Preparation and characterization of iridium dioxide-carbon nanotube nanocomposites for supercapacitors. *Nanotechnology* **2011**, *22*, 115706.
19. Yuan, C.; Zhang, X.; Su, L.; Gao, B.; Shen, L. Facile synthesis and self-assembly of hierarchical porous NiO nano/micro spherical superstructures for high performance supercapacitors. *J. Mater. Chem.* **2009**, *19*, 5772–5777.
20. Xu, J.; Cao, X.; Sun, L.; He, Y. Ordered mesoporous carbon/cobalt oxide composites as the electrode materials for supercapacitor. *Adv. Mater.* **2011**, *239–242*, 1026–1029.
21. Liu, Y.; Jiao, Y.; Zhang, Z.; Qu, F.; Umar, A.; Wu, X. Hierarchical SnO₂ nanostructures made of intermingled ultrathin nanosheets for environmental remediation, smart gas sensor, and supercapacitor applications. *ACS Appl. Mater. Interfaces* **2014**, *6*, 2174–2184.
22. Qu, Q.; Zhang, P.; Wang, B.; Chen, Y.; Tian, S.; Wu, Y.; Holze, R. Electrochemical Performance of MnO₂ Nanorods in Neutral Aqueous Electrolytes as a Cathode for Asymmetric Supercapacitors. *J. Phys. Chem. C* **2009**, *113*, 14020–14027.
23. Ghodbane, O.; Pascal, J.; Charles, I.; Montpellier, G.; Cnrs, U.M.R.; Aime, E. Microstructural Effects on Charge-Storage Properties in MnO₂-Based Electrochemical. *ACS Appl. Mater. Interfaces* **2009**, *1*, 1130–1139. [[PubMed](#)]
24. Miller, J.R.; Simon, P.; Patrice, S. Electrochemical Capacitors for Energy Management. *Sci. Mag.* **2008**, *321*, 651–652.
25. Toupin, M.; Brousse, T.; Bélanger, D. Charge storage mechanism of MnO₂ electrode used in aqueous electrochemical capacitor. *Chem. Mater.* **2004**, *16*, 3184–3190.
26. Reddy, R.N.; Reddy, R.G. Sol-gel MnO₂ as an electrode material for electrochemical capacitors. *J. Power Sources* **2003**, *124*, 330–337.
27. Wang, X.; Wang, X.; Huang, W.; Sebastian, P.J.; Gamboa, S. Sol-gel template synthesis of highly ordered MnO₂ nanowire arrays. *J. Power Sources* **2005**, *140*, 211–215.
28. Pang, S.C.; Anderson, M.A.; Chapman, T.W. Novel electrode materials for thin-film ultracapacitors: Comparison of electrochemical properties of sol-gel-derived and electrodeposited manganese dioxide. *J. Electrochem. Soc.* **2000**, *147*, 444–450.
29. Hegde, A.C. Effect of surfactant on high capacitance of galvanostatically deposited MnO₂. *J. Electroanal. Chem.* **2012**, *676*, 35–39.
30. Boukmouche, N.; Azzouz, N.; Bouchama, L.; Daltin, A.L.; Chopart, J.P.; Bouznit, Y. Supercapacitance of MnO₂ films prepared by pneumatic spray method. *Mater. Sci. Semicond. Process.* **2014**, *27*, 233–239.
31. Subramanian, V.; Zhu, H.; Vajtai, R.; Ajayan, P.M.; Wei, B. Hydrothermal synthesis and pseudocapacitance properties of MnO₂ nanostructures. *J. Phys. Chem. B* **2005**, *109*, 20207–20214.
32. Al-falahi, A.H. Structural and Optical Properties of MnO₂: Pb Nanocrystalline Thin Films Deposited by Chemical Spray Pyrolysis. *OSRG J. Eng.* **2013**, *3*, 52–57.
33. Hsu, C.; Chang, S.J.; Lin, Y.R.; Li, P.C.; Lin, T.S.; Tsai, S.Y.; Lu, T.H.; Chen, I.C. Ultraviolet photodetectors with low temperature synthesized vertical ZnO nanowires. *Chem. Phys. Lett.* **2005**, *416*, 75–78.
34. Qian, W.; Sun, F.; Xu, Y.; Qiu, L.; Liu, C.; Wang, S.; Yan, F. Human hair-derived carbon flakes for electrochemical supercapacitors. *Energy Environ. Sci.* **2013**, *7*, 379–386.

35. Fan, Z.; Yan, J.; Wei, T.; Zhi, L.; Ning, G.; Li, T.; Wei, F. Asymmetric supercapacitors based on graphene/MnO₂ and activated carbon nanofiber electrodes with high power and energy density. *Adv. Funct. Mater.* **2011**, *21*, 2366–2375.
36. Lu, X.; Zheng, D.; Zhai, T.; Liu, Z.; Huang, Y.; Xie, S.; Tong, Y. Facile synthesis of large-area manganese oxide nanorod arrays as a high-performance electrochemical supercapacitor. *Energy Environ. Sci.* **2011**, *4*, 2915.
37. Wang, B.; Li, H.; Liu, Q.; Wang, J.; Yu, L.; Yan, H.; Li, Z.; Wang, P. Optimizing the charge transfer process by designing Co₃O₄@PPy@MnO₂ ternary core-shell composite. *J. Mater. Chem. A* **2014**, *2*, 12968–12973.
38. Hsu, Y.-K.; Chen, Y.-C.; Lin, Y.-G.; Chen, L.-C.; Chen, K.-H. Birnessite-type manganese oxides nanosheets with hole acceptor assisted photoelectrochemical activity in response to visible light. *J. Mater. Chem.* **2012**, *22*, 2733.
39. Chigane, M.; Ishikawa, M. Manganese Oxide Thin Film Preparation by Potentiostatic Electrolyses and Electrochromism. *J. Electrochem. Soc.* **2000**, *147*, 2246–2251.
40. Hu, C.; Chen, E.; Lin, J. Capacitance and textural characteristics of polyaniline-platinum composite films. *Electrochim. Acta* **2002**, *47*, 2741–2749.
41. Suntivich, J.; Gasteiger, A.; Yabuuchi, N.; Nakanishi, H.; Goodenough, J.; Shao-Horn, Y. Design principles for oxygen-reduction activity on perovskite oxide catalysts for fuel cells and metal–air batteries. *Nat. Chem.* **2011**, *3*, 546–550.
42. Suntivich, J.; May, K.J.; Gasteiger, H.A.; Goodenough, J.B.; Shao-Horn, Y. A perovskite oxide optimized for oxygen evolution catalysis from molecular orbital principles. *Science* **2011**, *334*, 1383–1385.
43. Chen, K.; Wang, M.; Li, G.; He, Q.; Liu, J.; Li, F. Spherical α -MnO₂ Supported on N-KB as Efficient Electrocatalyst for Oxygen Reduction in Al–Air Battery. *Materials* **2018**, *11*, 601–615.
44. Hu, X.; Zhu, S.; Huang, H.; Zhang, J.; Xu, Y. Controllable synthesis and characterization of α -MnO₂ nanowires. *J. Cryst. Growth* **2016**, *434*, 7–12.
45. Li, D.; Leung, Y.H.; Djurišić, A.B.; Liu, Z.T.; Xie, M.H.; Gao, J.; Chan, W.K. CuO nanostructures prepared by a chemical method. *J. Cryst. Growth* **2005**, *282*, 105–111.
46. Brunauer, S.; Deming, L.; Deming, W.; Teller, E. On a theory of the van der Waals adsorption of gases. *J. Am. Chem. Soc.* **1940**, *62*, 1723–1732.
47. Rouquerol, J.; Avnir, D.; Fairbridge, W.; Everett, D.H.; Haynes, J.H.; Pernicone, N.; Ramsay, J.D., F.; Sing, K.S., W.; Unger, K.K. Recommendations for the characterization of porous solids. *Pure Appl. Chem.* **1994**, *66*, 1739–1758.
48. Sawangphruk, M.; Srimuk, P.; Chiochan, P.; Krittayavathananon, A.; Luanwuthi, S.; Limtrakul, J. High-performance supercapacitor of manganese oxide/reduced graphene oxide nanocomposite coated on flexible carbon fiber paper. *Carbon* **2013**, *60*, 109–116.
49. Kuo, S.-L.; Wu, N.-L. Investigation of Pseudocapacitive Charge-Storage Reaction of MnO₂·nH₂O Supercapacitors in Aqueous Electrolytes. *J. Electrochem. Soc.* **2006**, *153*, A1317.
50. Yin, B.; Zhang, S.; Jiang, H.; Qu, F.; Wu, X. Phase-controlled synthesis of polymorphic MnO₂ structures for electrochemical energy storage. *J. Mater. Chem. A* **2015**, *3*, 5722–5729.
51. Lee, H.Y.; Goodenough, J.B. Supercapacitor Behavior with KCl Electrolyte. *J. Solid State Chem.* **1999**, *144*, 220–223.
52. Wang, Y.T.; Lu, A.H.; Zhang, H.L.; Li, W.C. Synthesis of Nanostructured mesoporous manganese oxides with three-dimensional frameworks and their application in supercapacitors. *J. Phys. Chem. C* **2011**, *115*, 5413–5421.
53. Subramanian, V.; Zhu, H.; Wei, B. Nanostructured MnO₂: Hydrothermal synthesis and electrochemical properties as a supercapacitor electrode material. *J. Power Sources* **2006**, *159*, 361–364.
54. Zhang, X.; Zhao, D.; Zhao, Y.; Tang, P. High performance asymmetric supercapacitor based on MnO₂ electrode in ionic liquid electrolyte. *J. Mater. Chem. A* **2013**, *1*, 3706–3712.
55. Lang, X.; Hirata, A.; Fujita, T.; Chen, M. Nanoporous metal/oxide hybrid electrodes for electrochemical supercapacitors. *Nat. Nanotechnol.* **2011**, *6*, 232–236.

56. Zhu, G.; Deng, L.; Wang, J.; Kang, L.; Liu, Z.H. Hydrothermal preparation and the capacitance of hierarchical MnO₂ nanoflower. *Colloids Surfaces A Physicochem. Eng. Asp.* **2013**, *434*, 42–48.
57. Toupin, M.; Brousse, T.; Belanger, D. Influence of Microstructure on the Charge Storage Properties of Chemically Synthesized Manganese Dioxide. *Chem. Mater.* **2002**, *14*, 3946–3952.
58. Xiao, W.; Xia, H.; Fuh, J.; Lu, L. Growth of single-crystal α -MnO₂ nanotubes prepared by a hydrothermal route and their electrochemical properties. *J. Power Sources* **2009**, *193*, 935–938.
59. Li, Y.; Xie, H.; Wang, J.; Chen, L. Preparation and electrochemical performances of α -MnO₂ nanorod for supercapacitor. *Mater. Lett.* **2011**, *65*, 403–405.
60. Qiu, K.; Lu, Y.; Zhang, D.; Cheng, J.; Yan, H.; Xu, J.; Liu, X.; Kim, J.K.; Luo, Y. Mesoporous, hierarchical core/shell structured ZnCo₂O₄/MnO₂ nanocone forests for high-performance supercapacitors. *Nano Energy* **2015**, *11*, 687–696.
61. Hung, C.; Lin, P.; Tseng, T. High energy density asymmetric pseudocapacitors fabricated by graphene/carbon nanotube/MnO₂ plus carbon nanotubes nanocomposites electrode. *J. Power Sources* **2014**, *259*, 145–153.
62. Kundu, M.; Liu, L. Direct growth of mesoporous MnO₂ nanosheet arrays on nickel foam current collectors for high-performance pseudocapacitors. *J. Power Sources* **2013**, *243*, 676–681.
63. Zhao, Y.; Jiang, P.; Xie, S.S. Short communication ZnO-template-mediated synthesis of three-dimensional coral-like MnO₂ nanostructure for supercapacitors. *J. Power Sources* **2013**, *239*, 393–398.
64. Xu, C.; Zhao, Y.; Yang, G.; Li, F.; Li, H. Mesoporous nanowire array architecture of manganese dioxide for electrochemical capacitor applications. *Chem. Commun.* **2009**, *48*, 7575–7577.
65. Yang, S.; Yan, P.; Li, Y.; Cheng, K.; Ye, K.; Zhang, C.; Cao, D.; Wang, G.; Li, Q. Reduced graphene oxide decorated on MnO₂ nanoflakes grown on C/TiO₂ nanowire arrays for electrochemical energy storage. *RSC Adv.* **2015**, *5*, 87521–87527.
66. Naoi, K.; Simon, P. New Materials and New Configurations for Advanced Electrochemical Capacitors. *J. Electrochem. Soc.* **2008**, *17*, 34–37.
67. Yu, G.; Hu, L.; Liu, N.; Wang, H.; Vosgueritchian, M.; Yang, Y.; Cui, Y.; Bao, Z. Enhancing the supercapacitor performance of graphene/MnO₂ nanostructured electrodes by conductive wrapping. *Nano Lett.* **2011**, *11*, 4438–4442.
68. Lokhande, C.; Dubal, D.; Joo, O. Metal oxide thin film based supercapacitors. *Curr. Appl. Phys.* **2011**, *11*, 255–270.
69. Ke, B.; Wang, J.; Li, D.; Zhao, S.; Luo, L.; Yu, L.; Hussain, S. Electrochemical properties of hollow MnO₂ nanostructure: Synthesis and application. *J. Mater. Sci. Mater. Electron.* **2016**, *1–8*, 418–425.
70. Qu, D. The study of the proton diffusion process in the porous MnO₂ electrode. *Electrochim. Acta* **2004**, *49*, 657–665.
71. Aravinda, L.S.; Nagaraja, K.K.; Nagaraja, H.S.; Bhat, K.U.; Bhat, B.R. ZnO/carbon nanotube nanocomposite for high energy density supercapacitors. *Electrochim. Acta* **2013**, *95*, 119–124.
72. Wang, G.; Zhang, L.; Zhang, J. A review of electrode materials for electrochemical supercapacitors. *Chem. Soc. Rev.* **2012**, *41*, 797–828.
73. Xu, M.W.; Zhao, D.D.; Bao, S.J.; Li, H.L. Mesoporous amorphous MnO₂ as electrode material for supercapacitor. *J. Solid State Electrochem.* **2007**, *11*, 1101–1107.
74. Srither, S.R.; Karthik, A.; Arunmetha, S.; Murugesan, D.; Rajendran, V. Electrochemical supercapacitor studies of porous MnO₂ nanoparticles in neutral electrolytes. *Mater. Chem. Phys.* **2016**, *183*, 375–382.
75. Wang, H.-Q.; Chen, J.; Hu, S.J.; Zhang, X.H.; Fan, X.P.; Du, J.; Huang, Y.G.; Li, Q.Y. Direct growth of flower-like 3D MnO₂ ultrathin nanosheets on carbon paper as efficient cathode catalyst for rechargeable Li-O₂ batteries. *RSC Adv.* **2015**, *5*, 72495–72499.
76. Yang, L.C.; Zhong, Z.W.; Liu, J.W.; Gao, Q.S.; Hu, R.Z.; Zhu, M. Hierarchical MoO₂/N-doped carbon heteronanowires with high rate and improved long-term performance for lithium-ion batteries. *J. Power Sources* **2016**, *306*, 78–84.

77. Augustyn, V.; Come, J.; Lowe, M.A.; Kim, J.W.; Taberna, P.; Tolbert, S.H.; Abruña, H.D.; Simon, P.; Dunn, B. High-rate electrochemical energy storage through Li⁺ intercalation pseudocapacitance. *Nat. Mater.* **2013**, *12*, 518–522.
78. Kim, H.; Cook, J.; Lin, H.; Ko, J.; Tolbert, S.; Dunn, B. Oxygen vacancies enhance pseudocapacitive charge storage properties of MoO_{3-x}. *Nat. Mater.* **2016**, *16*, 454–460.

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