

ZnO/MnO_x Nanoflowers for High-Performance Supercapacitor Electrodes

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heterostructured composite. The effect of the MnO_x coating on the performance of the nanocomposite was analyzed by comparing the performance of supercapacitors employing ZnO and the ZnO/ MnO_x nanocomposites. The ZnO/ MnO_x nanocomposites exhibited excellent current rate capability and an excellent capacitance of 556 F·g⁻¹ at a current density of 1 A·g⁻¹. The optimized ZnO/ MnO_x NF electrode presented a remarkable long-term cycling stability, with a capacitance retention of 96% after 10,000 cycles. In a coin cell assembly, at an operating voltage of 0.9 V, the energy density of the optimized supercapacitor cell was 16



Wh·kg,⁻¹ at a power density of 225 W·kg⁻¹. Becasue of its excellent electrochemical performance, the optimized ZnO/MnO_x NF composite electrode is promising for high-energy-density supercapacitor applications.

KEYWORDS: Electrodeposition, Nanoflowers, Nickel nanocones, Supercapacitor, Energy storage

INTRODUCTION

High-capacitance materials are used to enhance the energy storage and rate capability of metal oxide pseudocapacitors. These active materials with new morphologies are essential for exploring surface reactions in the discovery of better energy storage sites.¹⁻⁴ Oxides of transition metals, such as Ru,⁵ Mn,^{8,9} Fe,^{10,11} and Sn, in various oxidation states, have been widely studied owing to their high pseudocapacitance. In addition, ZnO and MnO2 are very promising oxides owing to their environmental friendliness, natural abundance, and ideal capacitive characteristics.¹²⁻¹⁵ Moreover, these oxides have demonstrated the ability to self-assemble in various nanostructured morphologies. Furthermore, electrodes with nanostructured morphologies may exhibit significantly enhanced electrochemical performance owing to the shorter diffusion pathways, rapid charge carrier transfer, and greater number of electrochemically active sites.¹⁶⁻¹⁸

 MnO_x presents a high specific capacitance within a 1 V potential window in neutral electrolytes, which are known as green electrolytes.^{19,20} However, the poor conductivity of such electrolytes limits the exploitation of their full potential.^{21–23} Hence, MnO_x is typically loaded onto ZnO scaffolds; this enhances the redox activity and provides faster electron transport.²⁴ Such ZnO/MnO_x composite electrodes have been synthesized via electrodeposition,²⁵ hydrothermal methods,²⁶ and electrospinning.²⁷ Among these techniques,

electrochemical deposition is advantageous for tuning the morphology of the film in which the parameters, such as the composition of the electrolyte, applied current density or potential, electrodeposition time, and the electrode surface, can be controlled.²⁸ In addition to the use of electrodes with textured morphology, the use of three-dimensional (3D) metal foams as substrates for the deposition of nanostructured supercapacitor materials has attracted significant attention.^{21,29} Such 3D substrates provide high contact areas for the nanostructured material and thus enhance the electrolyte/ electrode interface; this results in faster electron transport and higher charge storage.^{30,31} In one approach, Cu substrates were first electroplated with Ni nanocones (NCs), which provided a textured surface for the deposition of ZnO/MnO_x. The nickel nanocones are designed to facilitate the injection of electrolyte ions, which accelerates the electrochemical reactions and consequently increases the energy storage capacity.³²

In this study, we demonstrate the facile synthesis of ZnO and ZnO/MnO_x nanoflowers (NFs) using a cost-effective

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electrodeposition technique. The electrochemical characteristics of the ZnO/MnO_x composite electrodes, the effect of the K₂SO₄ concentration, and also that of the fixed zinc salt concentration are investigated to determine the suitability of the electrodes for supercapacitor applications. The nanothin petals of the active material provide many electrochemically active sites for high energy storage. The ZnO/MnO_x NFs exhibit remarkable capacitance, excellent current rate capability, and exceptional long-term stability, indicating that the optimized electrode is a very promising material for highenergy-density supercapacitor applications. The ZnO NFs are coated with MnO_x to improve their long-term cycling stability as a parameter of the electrochemical performance. The ZnO NFs are intentionally grown on Cu foil electroplated with Ni NCs, which is expected to increase the surface area and electrical contact of the nanostructure, consequently affording high specific capacitance.

EXPERIMENTAL SECTION

Preparation of Ni NCs. Ni foil and Cu foil $(3 \text{ cm} \times 4 \text{ cm})$ were cleaned using acetone and ethanol. The foils were maintained in an ultrasonic bath for 10 min to remove the ultrathin oxide layers, grease, and other impurities on their surface. Ni NCs were then deposited on the cleaned Cu substrates. Ni foil was used as the anode, and another piece of Cu foil was used as the cathode for deposition of the Ni NCs. To obtain the electroplating solution, 20 g of nickel(II) chloride hexahydrate (NiCl 6H2O) was first dissolved in 80 mL water at 60 °C. Thereafter, 10 g of boric acid (H₃BO₃) was dissolved in 80 mL of water at 60 °C. These solutions were combined to form a milky green mixture. To adjust the pH, 2 mL of ammonium hydroxide (NH4OH) was diluted with 20 mL of water, and 2 mL of concentrated HCl was diluted with 20 mL of water. The mixed NH₄OH and HCl solution was then added to the NiCl 6H2O and H2BO2 solution. Addition of a buffer agent (H₃BO₃) to NiCl·6H₂O is essential for controlling the adverse reaction of the Ni salt upon addition of the mixed solution of NH4OH and HCl. H3BO3 is a weak acid-forming nickel-borate complex that enhances metal deposition. The pH of the NiCl·6H₂O solution (200 mL) was determined to be 6. NH₄OH and HCl were used to adjust the pH of the solution to 6 to accelerate metal deposition and facilitate growth of the nickel nanocones. This solution was used as the electrolyte, and Ni foil was used as the electrode to coat the Cu foil with Ni NCs by electrodeposition for 6 min at the current density of 10 mA·cm⁻². All chemicals were purchased from Sigma-Aldrich and were used as received. The nickel nanocones were

fabricated by electrodeposition, as illustrated in Scheme 1. The nickel nanocones provide a significant improvement in the electrical conductivity and protect the nanostructures of the ZnO nanoflowers.³³

Electrodeposition of ZnO over Ni NCs and MnO, over ZnO via Chemical Bath Deposition. For the electrodeposition of ZnO, 90 mL of aqueous 0.1 M zinc acetate dihydrate (Zn(CH₃COO)₂. 2H₂O, ZnAc, Sigma-Aldrich) with 0.05 M potassium sulfate (K₂SO₄, Sigma-Aldrich) was prepared. The pH of the solution was adjusted to 6 by adding 0.2 mL nitric acid. In addition, the concentration of $\mathrm{K}_2\mathrm{SO}_4$ was varied as 0.05, 0.1, 0.15, and 0.2 M to evaluate the concentration dependence of the nanostructure of the ZnO NFs. Electrodeposition was conducted using a two-electrode setup, and the ZnAc/K₂SO₄ solutions were used as electrolytes (Scheme 1). The Ni NC-coated Cu foil and a Pt wire were used as the working and counter electrodes, respectively. ZnO was electrodeposited at the constant current density of 3 mA·cm⁻² for 5 min. The ZnO-coated Ni NC/Cu substrates were rinsed with deionized water and dried using N_2 gas, followed by annealing in a tube furnace at 400 $^\circ \mathrm{C}$ for 10 min to remove impurities and to improve the crystallinity of the samples. The samples obtained using the 0.05, 0.10, 0.15, and 0.20 M K₂SO₄ solutions are hereafter referred to as A, B, C, and D, respectively. The nanoflower morphology of ZnO is depicted in Scheme 1 (see part II).

The optimal ZnO NF sample (sample C) was coated with MnO_x to improve the long-term cycling stability as a parameter of the electrochemical performance. To deposit MnO_x over the annealed ZnO NFs via chemical bath deposition (CBD), a 1 mM aqueous solution of potassium permanganate (Sigma-Aldrich) was prepared, and the ZnO-coated annealed NF films were soaked in this solution for 60 min. During the CBD process, the temperature was maintained at 150 °C. Subsequently, the films were rinsed, dried, and annealed, as described above. As shown in Scheme 1, the annealed ZnO/MnO_x electrodes were illuminated with a light-emitting diode (LED) under 20 mA current and 2 V forward voltage. The physical dimensions of the electrodes were 1.2 cm \times 3 cm.

Physicochemical Characterization of ZnO/MnO_x Films. The morphology of the samples was analyzed using scanning electron microscopy (SEM; S-5000, Hitachi, Ltd.) and transmission electron microscopy (TEM; JEM 2100F, JEOL Inc.). Energy-dispersive X-ray spectroscopy (EDS), SEM, and TEM analyses were used to determine the elemental distribution in the samples. The crystalline phases of the samples were determined using an X-ray diffractometer (XRD, SmartLab, Rigaku). The chemical states of the ZnO/MnO_x films were evaluated using X-ray photoelectron spectroscopy (XPS; Theta Probe Base System, Thermo Fisher Scientific Co.).

Electrochemical Characterization during Supercapacitor Testing. The fabricated electrodes were evaluated by electrochemical characterization methods: Cyclic voltammetry (CV) was onducted in a three-electrode configuration using a VersaSTAT-3 (Princeton Applied Research, USA) potentiostat/galvanostat, and galvanostatic charge/discharge (GCD) tests were performed in a two-electrode configuration by assembling the supercapacitor electrodes in 2032 coin-type cells, using a WBCS 3000 (WonATech, Seoul, South Korea) battery cell test system. An electrochemical impedance spectroscopy (EIS; VersaSTAT-3, Princeton Applied Research, USA) system was used to analyze the performance and sustainability of the fabricated electrodes for supercapacitor applications. Symmetric 2032 coin cells were prepared using the standard procedure in which the circular electrodes (14 mm in diameter) were separated using a polymer separator, and 1 M Na₂SO₄ was used as the electrolyte. The current collector was made of copper, which was electroplated with nickel. The accuracy of the sample weight was ensured by confirming the repeatability of the sample fabrication in 10 replicate measurements. The controlling parameters for the electrodeposition process are time, sample size, distance between the electrodes, and solution temperature. All of these parameters were kept constant to ensure the repeatability of the sample fabrication. The CV and GCD tests were performed within different potential windows at room temperature (20 °C). The EIS measurements were performed at a very small perturbation voltage of 10 mV over the frequency range from 100 kHz to 0.1 Hz.

RESULTS AND DISCUSSION

Morphological Characterization of ZnO/MnO_x NFs. The Cu substrates were electroplated with Ni NCs, and the surface morphology of the Ni NCs is presented in Figure S1. The SEM images of the ZnO NFs that were electrodeposited using the K_2SO_4 solutions of different concentrations, used as the electrolyte (Figure 1), illustrate the essential role of K_2SO_4 in forming thin petals and numerous NFs. When the concentration of the K₂SO₄ solution was low, i.e., 0.05 and 0.1 M, growth of the NFs was incomplete, as indicated by the large spaces between the NFs. In contrast, the use of 0.15 and 0.2 M K_2SO_4 solutions led to rapid growth of the nanosheets



Figure 1. Scanning electron microscopy image of ZnO deposited using electrolytes with different K_2SO_4 concentrations: (a), (b) 0.05, (c), (d) 0.10, (e), (f) 0.15, and (g), (h) 0.20 M.

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and significantly smaller voids (Figures 1e–h). Consequently, this increased the electrolyte/electrode interfacial area, enhancing the energy storage of the nanosheets. The atomic force microscopy (AFM) images of the various ZnO NF samples are shown in Figure S4. The roughness (R_a) of these samples increased with increasing K₂SO₄ concentration; $R_a = 0.24$, 0.38, 0.43, and 0.46 μ m with corresponding concentrations of 0.05, 0.10, 0.15, and 0.20 M, respectively. The NF morphology of ZnO was attributed to the optimal annealing of the samples in air at 400 °C. Given that sample C was fully covered in NFs and based on the CV data (see the Cyclic Voltammetry Analysis of ZnO/MnOx NFs section), the 0.15 M K₂SO₄ solution was considered optimal for obtaining ZnO NFs.

The formation of ZnO NFs instead of other nanostructures, such as nanorods or nanoplates, is attributed to the interaction of the SO_4^{2-} anions with the positive Zn^{2+} ions and suppression of the growth of ZnO in multiple planes. The presence of various ions in the electrolyte during electrodeposition controls the growth of the ZnO nanostructures in a certain direction. When the K₂SO₄ concentration is low, the hydroxyl ion generation rate is high, facilitating the precipitation of $Zn(OH)_2$ in which the anions rapidly react with Zn²⁺. This process leads to oriented growth of the nanostructure. Conversely, when the K₂SO₄ concentration is high, the precipitation process slows, during which SO⁴⁻ ions are adsorbed at the (002) surface, leading to the capping effect. With the increase in the concentration of K_2SO_4 , the number of SO_4^{2-} ions also increases. This led to the growth of $Zn(OH)_{4}^{2-}$ in the (0001), (0110), (1011), (1011), (0001), and $(01\overline{1}0)$ planes, resulting in the formation of shorter nanopetals. Thus, the combined capping effect of the SO⁴⁻ ions and the reduced precipitation of $Zn(OH)_2$ resulted in the plate-type morphology.^{34,3}

 MnO_x was deposited over the ZnO NFs (sample C) via CBD to increase the capacitance of the supercapacitor electrode. The SEM images in Figure 2a and b illustrate the



Figure 2. (a) High-magnification and (b) low-magnification scanning electron microscope images of ZnO/MnO_x nanoflowers.

morphology of the ZnO/MnO_x NFs. ZnO/MnO_x NFs with ultrathin petals can be observed in the high-magnification SEM image in Figure 2a. A few micrometer-sized gaps between the nanosheets and nanopetals were readily visible (Figure 2a); these gaps could facilitate the permeation of the electrolyte. Increased electrolyte penetration could significantly increase the number of electrochemically active sites for energy storage.

Structural Characterization of ZnO/MnO_x **NFs.** The crystalline structure of the ZnO nanosheets obtained using K_2SO_4 solutions of different concentrations was analyzed by XRD (Figure S2). The peaks at 38°, 45°, 51°, and 75° in the XRD patterns of the ZnO nanosheets are attributed to the (110), (111), (200), and (220) planes, respectively, of the Ni NC substrate (JPCDS No. 04-0850). In addition, the peaks at 43° and 49° are ascribed to the (111) and (200) planes, respectively, of the Cu substrate (JPCDS No. 04-0836). The



Figure 3. (a) X-ray diffraction pattern and (b) Zn 2p, (c) Mn 2p, and (d) O 1s core-level X-ray photoelectron spectra of ZnO/MnO_x NFs. Here, O_{ads} , O_{ads} , O_{ads} , O_{M-O} denote O adsorbed from the ambient moisture, O adsorbed on the surface of the sample metal, and bound oxygen, respectively.

electrodeposited ZnO adopted the wurtzite polycrystalline structure, where the peaks at 32°, 34°, and 36° in the XRD spectrum correspond to the (100), (002), and (101) planes (JPCDS No. 36-1451), respectively. The crystallinity of ZnO was found to decrease as the concentration of K₂SO₄ increased because increasing the number of SO₄²⁻ ions could retard the growth of the ZnO crystals in a particular direction. Furthermore, the XRD pattern of the ZnO/MnO_x NFs obtained by depositing MnO_x over sample C exhibited no MnO_x peaks (Figure 3a); this is attributed to the low concentration of Mn in these NFs.

The chemical states of the elements comprising the ZnO/ MnO_x NFs were examined using XPS. The characteristic peaks of Zn, O, and Mn were identified in the survey spectra of the ZnO/MnO_x NFs deposited on the Ni NC/Cu substrate (Figure S3), where the characteristic peak of C is attributed to the presence of ambient C during testing. The core-level Zn, Mn, and O XPS profiles are illustrated in Figure 3b, c, and d, respectively. The two peaks at binding energies of 1022.2 and 1044.8 eV in the core-level Zn 2p spectrum correspond to Zn $2p_{3/2}$ and Zn $2p_{1/2}$, respectively, with a spin-orbit splitting of 23.3 eV, showing good agreement with the reported data for Zn^{2+.36} The core-level Mn 2p spectrum in Figure 3c exhibits two characteristic peaks at 641.9 and 654.7 eV. The spin-orbit splitting of the Mn 2p peak doublet was 12.8 eV.37-41 A similarly high spin-orbit splitting was also reported by Luo et al.⁴² for a sample containing only 1 atom % Mn, which suggests that the Mn2+ state was predominant. The concentration of potassium permanganate used in the experiment was 0.1 mM, which produced 1.4 atom % Mn in the sample based on the EDAX results shown in Figure S5. Each peak could be further deconvoluted into three peaks, indicating that Mn was present

in multivalent states (Mn^{2+} , Mn^{3+} , and Mn^{4+}), the relative contents of which were 49.5%, 27.4%, and 23.1%, respectively.^{19,43} The absence of the lower binding energy peak from the Mn 2p spectrum suggests that no metallic Mn was present in the sample. The O 1s peaks of the ZnO/MnO_x NFs could be deconvoluted into three peaks at 529.9, 531.2, and 532.4 eV. The peak at the lowest binding energy (529.9 eV) (Figure 3d) is attributed to the formation of metal-bonded oxygen (O^{M-O}) species, wherein the "bonded oxygen" implies oxygen molecules bonded with metals (Mn and/or Zn cations), denoted as Mn-O and Zn-O. The binding energies of Mn-O and Zn-O were 529.5 and 529.7 eV, respectively. These energy values are extremely close and were thus difficult to differentiate. The low-energy oxygen atoms bonded to Mn/Zn satisfy the stoichiometric oxidation state (see the deconvoluted curve in Figure 3d). Furthermore, the peak at the medium binding energy of 531.2 eV is ascribed to the surface oxygen, i.e., to O^{2-}/O^{-} species, associated with the functional groups such as CO_3^{2-} , which were formed due to the O-deficient areas on the sample. The peak at 532.4 eV is attributed to the loosely bound O adsorbed on the surface from the ambient moisture.44,45 The results of the XRD and XPS analyses confirm the formation of ZnO/MnO_x NFs on the Ni NC/Cu substrate.46

The focused ion beam image of the ZnO/MnO_x sample is depicted in Figure 4a. Figure 4b presents a cross-sectional lowmagnification TEM image of the MnO_x -coated ZnO nanosheets. The high-resolution transmission electron microscopy (HRTEM) image in the inset of Figure 4b was obtained from the area marked with the yellow square and illustrates some lattice fringes; however, these fringes are difficult to distinguish. The selected area electron diffraction pattern in



Figure 4. (a) Focused ion beam image and (b) low-magnification transmission electron microscopy (TEM) image of ZnO/MnO_x NFs (high-resolution TEM image in inset), (c) selected area electron diffraction pattern (SAED), and (d) high-magnification TEM image of ZnO/MnO_x and elemental maps of Zn, Mn, and O of ZnO/MnO_x sample.

Figure 4c presents the diffraction rings indexed to the (103) and (102) planes of wurtzite ZnO and the (200) plane of MnO_x . The high-magnification TEM image of ZnO/MnO_x in Figure 4d and the corresponding elemental maps indicate the presence of Zn, Mn, and O, attributed to the ZnO nanosheets coated with MnO_x , which confirms that the NF petals comprised ZnO/MnO_x .

Cyclic Voltammetry Analysis of ZnO/MnO_x NFs. The applicability of the heterostructured ZnO/MnO_x NF electrodes for supercapacitors was demonstrated using CV measurements. Figure 5 presents the CV data for ZnO and the ZnO/ MnO_x NFs. The electrochemical performance of the electrodes was not affected by the presence of Cu or Ni because the contribution of these ions to the current was negligible, as illustrated by the CV curves in Figure S6. The CV curves (scan rate, 100 mV·s⁻¹) of the supercapacitor electrodes deposited using various K₂SO₄ concentrations and a predetermined amount of ZnAc are presented in Figure 5a. The variations in the CV curves are attributed to the changes in the morphology of the electrodes. It was evident that higher concentrations of K₂SO₄ in the precursor solution resulted in morphological deformation (Figure 1d), which reduced the current response of sample D based on the CV curve. Moreover, the ZnO samples presented a gradual and larger increase in the magnitude of the current after potential reversal. This phenomenon suggests that more Na^+ ions than SO_4^{2-} ions accumulated on the NF petals during the electrochemical process (because the ionic radius of Na+ is larger than that of SO₄²⁻), and therefore, the pseudocapacitive behavior was slightly distorted from the ideal characteristics. The CV curves of the ZnO NFs at various scan rates did not present quasirectangular shapes (Figure 5b), which is attributed to the large internal resistance of the NFs. The deviation of the CV curves of the ZnO NFs from the rectangular shape arises from the electrode resistivity, which intensifies the polarization of the accumulated charges. Such voltammograms suggest a lack of

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charge balance at the electrodes. Conversely, the symmetric CV curves remained unchanged, which is a typical characteristic of pseudocapacitance. However, no redox humps were observed, indicating that the sample presented pseudocapacitive behavior in the neutral electrolyte (1 M Na₂SO₄). The CV curves of the ZnO NFs in different potential windows presented the same shape (Figure 5c), demonstrating the good reversibility of the supercapacitor electrodes. The anodic and cathodic CV curves of the ZnO NFs in different potential windows presented slight variations, attributed to the internal resistance of the active material and charge accumulation during repeated CV measurements.

Figure 5d presents the quasi-rectangular CV curves of the ZnO/MnO_x NFs; the presence of MnO_x contributed significantly to the almost ideal pseudocapacitive characteristics of the NFs. The area under the curve of ZnO was smaller than that of ZnO/MnO_x ; moreover, the current polarity for the ZnO/MnO_x electrode changed immediately with a decrease in the potential (Figure 5). The shape of the CV curves remained unchanged with variation of the scan rate, and thus, it could be inferred that the samples presented excellent reversibility and remarkable electrochemical stability. Furthermore, we varied the potential window for the ZnO/MnO_r sample, and the obtained CV curves presented excellent anodic/cathodic matching current values at corresponding voltages (Figure 5e). Thus, it was concluded that the ZnO/ MnO_x NF sample released electrostatic charge more rapidly than the ZnO NF sample. The fast response capability could also be confirmed by plotting the peak current variation vs the square root of the scan rate (Figure 5f). The ZnO sample exhibited asymmetric anodic vs cathodic peak currents at each scan rate. However, the symmetry of the plot for the ZnO/ MnO_x sample was indisputable.

Moreover, when the peak current curves were extrapolated, the anodic and cathodic curves of ZnO crossed at approximately 1 mV^{0.5}·s^{-0.5}, and the value of the extrapolated peak current was -1.35 mA. Furthermore, the curves of the ZnO/MnO_x sample did not intersect at the origin when extrapolated. However, the peak current at the intersection point of the anodic/cathodic peak current (-0.16 mA) was less and close to the origin of the graph. Thus, the CV data in Figure 5d-f reveal that the ZnO/MnO_x electrodes presented excellent reversibility. The Faradaic redox reaction of ZnObased electrodes involves the intercalation of Na⁺ ions from the electrolyte into ZnO

$$ZnO + Na^{+} + e^{-} \rightleftharpoons ZnO - Na$$
 (1)

The NFs and voids between the petals allowed rapid intercalation and deintercalation of the Na⁺ ions. However, pristine ZnO was not suitable for long-term cycling as an electrode material for supercapacitor applications, owing to its corrosiveness and poor conductivity. Farzana et al. suggested that active materials that present voltammograms with a quasi-rectangular shape with mirror image characteristics are electrochemically stable.⁴⁷ Hence, protecting the ZnO sample and exploiting the capacitive characteristics of MnO_x would be advantageous, as illustrated by the CV data for the ZnO/MnO_x NFs (Figure 5d–f).

Supercapacitors generally operate by a Faradaic charge/ discharge mechanism, and electrostatic double-layer capacitance is generated at the electrode/electrolyte interface, which increases the current output during cathodic scanning. Moreover, the cyclic voltammograms of the ZnO/MnO_x NFs

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Figure 5. (a) Cyclic voltammetry (CV) curves of samples with different K_2SO_4 concentrations at a scan rate of 100 mV·s⁻¹. CV curves of sample C at (b) different scan rates and (c) in various potential windows. CV curves of the ZnO/MnO_x NF electrode (d) at different scan rates and (e) in various potential windows. (f) Peak current vs square of scan rate for CV curves shown in panel (d). Here, samples A, B, C, and D denote ZnO NF samples obtained using 0.05, 0.1, 0.15, and 0.2 M K_2SO_4 solutions, respectively.

were similar to those of carbon-capacitive electrodes. This similarity confirms that MnO, makes the ZnO/MnO, NFs pseudocapacitive. In general, an electrode exhibiting pseudocapacitance undergoes a continuous change in the charge (dQ)due to the electrochemical reaction. The voltammogram is rectangular in shape in a given potential window. The electrochemical reaction may abruptly change the charge flow, causing a sharp peak or signal to appear in the voltammogram. This sharp change violates the definition of the continuous function, and thus, the electrode is no longer considered pseudocapacitive. For the ZnO/MnO_x NFs, the high current during the reduction process (cathodic curve) could be attributed to the accumulation of more Na⁺ ions (lower ionic radius of \sim 116 pm) than SO₄²⁻ ions (higher ionic radius of ~258 pm) at the electrolyte/electrode interface. However, for the anodic curve, which was obtained during oxidation, fewer SO4²⁻ ions than Na⁺ ions accumulated at the electrolyte/electrode interface, owing to the larger ionic radius of the former, resulting in a lower current. The dominant reduction reaction observed for the ZnO NFs was also supported by the relationship between the peak current and scan rate. The peak currents for the anodic and cathodic curves, which reveal the electrokinetics, are illustrated in Figure

Sc. Furthermore, the peak currents of the anodic and cathodic curves were extrapolated (Figure 5f) to determine the characteristics of the electrode. The extrapolated peak anodic current curve did not pass through the origin, which indicates only partial diffusion of the SO_4^{2-} ions. However, when the cathodic peak current was extrapolated to a zero scan rate, it passed through the origin. Thus, during reduction, the electrode exhibited electrochemical quasi-reversibility, and the movement of the Na⁺ ions was entirely diffusion controlled.⁴⁸ In contrast, the ZnO/MnO_x NFs presented in Figure 5f generated symmetric anodic vs cathodic peak currents, leading to rapid and increased charge storage.

Galvanostatic Measurements for ZnO/MnO_x Electrodes. The electrochemical performance of the electrodes for supercapacitor applications was further investigated using GCD experiments. The GCD curves of the optimized ZnO NF electrode at current densities of 1, 1.5, 2, 3, and 5 A·g⁻¹ and in different potential windows are presented in Figure 6a– c. For the CV analysis, a three-electrode configuration was employed, with the ZnO/MnOx nanoflowers as the working electrode. For the CV analysis, the three-electrode configuration was employed, wherein the ZnO/MnOx nano-

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Figure 6. Galvanostatic charge/discharge (GCD) curves of sample C in potential windows of (a) 0-0.5, (b) 0-0.7, and (c) 0-0.9 V. (d) Comparison of GCD curves of sample C in various potential windows at $1 \text{ A} \cdot \text{g}^{-1}$. Potential window dependence of (e) capacitance at different current densities and (f) energy density at different power densities for sample C. Here, sample C denotes ZnO NFs obtained using a 0.15 M K₂SO₄ solution.

flowers were used as the working electrode, Pt wire as the counter electrode, and Ag/AgCl as the reference electrode. CV analysis was used to determine the potential range of the electrode. The specified voltage range is the electrode potential with respect to the reference electrode. For the galvanostatic charge/discharge tests, a symmetric capacitor configuration was used with two identical electrodes. During the galvanostatic measurement (0-0.9 V), zero was considered as the reference voltage for the measurement system, and the CV analysis was performed in the potential range from -0.9 to 0 V with respect to the reference voltage of -0.9 V vs AgAcl. In short, both systems measure the potential difference with respective reference voltages. The weights of the active materials (ZnO and ZnO/MnO_x) (Table 1) were used for the GCD measurements. The GCD curves at the current density of 1 A·g⁻¹ in different potential windows are illustrated in Figure 6d. The GCD curves of samples A, B, and D and their electrochemical responses at various current densities in the capacitance voltage range of 0-0.7 V are presented in Figure S7.

As expected, the charging and discharging times of the supercapacitor electrode increased as the potential window range increased. In addition, the charge and discharge cycles of the optimized ZnO NF electrode were nearly symmetrical and triangular in all potential windows, indicating that the electrode demonstrated a good capacitive GCD performance. Thus,

Table 1. Weight Variation of Electrodes duringElectrodeposition

Sample	Copper foil weight (g·cm ⁻²)	Cu/Nickel nanocone weight (g·cm ⁻²)	Total weight after annealing (g·cm ⁻²)	Total weight before annealing (g·cm ⁻²)
А	0.0289	0.0294	0.0302	0.0304
В	0.0289	0.0296	0.0304	0.0306
С	0.0289	0.0296	0.0305	0.0307
D	0.0289	0.0296	0.0305	0.0308
ZnO/MnO	0.0289	0.0296	0.0305	0.0307

from the GCD curves, it could be concluded that the optimized ZnO NF electrode was operational at voltages up to 0.9 V, which is consistent with the CV results.

To estimate the specific capacitance of the electrode material used during the galvanostatic measurements, eq 2 can be applied for the discharge section of the GCD curves (Figure 6a-c).^{49,50}

$$C_{\rm s} = \frac{4It_{\rm d}}{m\Delta V} \left(\mathbf{F} \cdot \mathbf{g}^{-1} \right) \tag{2}$$

where C_s is the specific capacitance of the electrode, *I* is the discharge constant current (A), t_d is the discharge time (s), *m* is the mass of active material (g), and ΔV is the potential window (V). C_s was calculated from the galvanostatic

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Figure 7. Galvanostatic charge/discharge (GCD) curves of ZnO/MnO_x nanoflowers (NFs) at various current densities in potential windows of (a) 0–0.5, (b) 0–0.7, and (c) 0–0.9 V. (d) Comparison of GCD curves of ZnO/MnO_x NFs in these potential windows at current density of 3 A·g⁻¹. (e) Potential window dependence of capacitance at different current densities. (f) Ragone plot (energy density vs power density).

discharge curve in the potential window excluding the IR drop, where IR, the internal resistance, is the ohmic drop (V) during the polarization reversal of the constant current.

Furthermore, using the calculated capacitance values, the specific energy (E) and power (P) of the supercapacitor cell could be estimated as follows:³⁸

$$E = \frac{C_{\rm s} \Delta V^2}{8 \times 3.6} \, (\text{Wh·kg}^{-1}) \tag{3}$$

$$P = \frac{3.6 \times E_{\rm s}}{t_{\rm d}} \, (\rm kW \cdot \rm kg^{-1}) \tag{4}$$

The specific capacitance of the ZnO NFs was calculated from the GCD curves acquired with variation of the potential window and current density; the results are presented in Figure 6e. Specific capacitances of 400 (0–0.9 V), 357 (0–0.7 V), and 294 (0–0.5 V) $\text{F} \cdot \text{g}^{-1}$ were obtained in the different capacitance potential ranges (CPRs) at the current density of 1 $\text{A} \cdot \text{g}^{-1}$. Specific capacitances of 211, 186, and 120 $\text{F} \cdot \text{g}^{-1}$ were obtained at the higher current density of 5 $\text{A} \cdot \text{g}^{-1}$ (Figure 6e) for the CPRs of 0–0.9, 0–0.7, and 0–0.5 V, respectively. The current rate capability of the specific capacitance retention at CPRs of 0.9 and 0.7 V approached approximately 52%, while the rate capability at lower CPR (0.5 V) was only 41%. Therefore, the morphology of the ZnO NFs significantly improved the current capability and stability of the supercapacitor electrodes. The performance of sample C was better than those of samples A and B; this is explained by the increased growth of the nanopetals of the ZnO nanoflowers. The SEM images in Figure 1a-d show that growth of the ZnO nanoflowers was incomplete at lower concentrations. At the optimal concentration of 0.15 M, the nanostructure of the ZnO nanoflowers was fully grown, as shown in Figure 1e-f. At the highest concentration of 0.20 M, the structure was overgrown, and an excessive number of voids was created, resulting in undesirable reduction of the electrode capacitance. The improved capacitance resulted in higher energy density of the supercapacitor electrodes in the corresponding capacitive voltage ranges. A high energy density of 13 $\text{Wh}{\cdot}\text{kg}^{-1}$ was achieved in the potential window of 0-0.9 V, at the power density of 225 W·kg⁻¹ (Figure 6f). Even at a higher power density (1125 W· kg⁻¹), the supercapacitor cell demonstrated an excellent energy density retention (7 $Wh \cdot kg^{-1}$).

GCD measurements of the ZnO/MnO_x NF electrodes were performed at current densities similar to those used for the ZnO NF electrodes. Figure 7a-c presents the charge/ discharge profiles in three potential windows. As MnO_x is known to be a good pseudocapacitive material, all GCD curves presented in Figure 7a-d were linear. Furthermore, the GCD curves acquired in the three potential windows were compared (Figure 7d). The ZnO/MnO_x NF electrodes presented triangular GCD profiles with almost zero internal resistance

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Materials	Capacitance	Current density	Potential window (V)	Rate capability (%)	Capacitance retention (%)/Number of cycles/Current density or Scan rate	Electrolyte	Energy density (Wh·kg ⁻¹)/Power density (W·kg ⁻¹)
ZnO/MnO ₂ Urchin ²⁶	262 $F \cdot g^{-1}$	$0.2 \ A \cdot g^{-1}$	0-0.8	59	$111/5000/2 \text{ A} \cdot \text{g}^{-1}$	0.5 M ^a	-
ZnO@amorphous ZnO-doped MnO ₂ ¹²	140 mF· cm ⁻²	$1.0 \text{ mA} \cdot \text{cm}^{-2}$	0-0.8	42	88/10,000/0.5 mA·cm ⁻²	5 M ^b	_
Graphene/ZnO ²⁰	$2.6 \text{ mF} \cdot \text{cm}^{-2}$	$0.2 \text{ mA} \cdot \text{cm}^{-2}$	0-1.6	55	86/10,000/0.57 mA·cm ⁻²	1 M^{c}	_
ZnO/MnO_2^{53}	$2.6 \text{ mF} \cdot \text{cm}^{-2}$	$1.0 \text{ mV} \cdot \text{s}^{-1}$	0-1.0	~9	$120/5000/20 \ \mu \text{A} \cdot \text{cm}^{-2}$	5 M ^b	_
ZnO/MnO^{54}	$14 \text{ mF} \cdot \text{cm}^{-2}$	$0.1 \text{ mA} \cdot \text{cm}^{-2}$	0-0.8	7	93/5000/5 mA·cm ⁻²	1 M^{a}	_
ZnO/ MnO ₂ Nanowire ²³	$501 \text{ F} \cdot \text{g}^{-1}$	$2.0 \text{ A} \cdot \text{g}^{-1}$	0-0.9	~22	$93/1000/100 \text{ mV} \cdot \text{s}^{-1}$	1 M ^a	63/950
ZnO/MnO ₂ core- shell ²²	424 $F \cdot g^{-1}$	$0.5 \text{ A} \cdot \text{g}^{-1}$	-0.2-0.8	36	$92/3000/5 \ A \cdot g^{-1}$	1 M ^a	-
ZnO@MnO ₂ nanocable ¹⁹	$613.5 \ F{\cdot}g^{-1}$	$1.0 \text{ A} \cdot \text{g}^{-1}$	0-0.9	60	$90/5000/5 \ A \cdot g^{-1}$	0.5 M ^a	-
ZnO/Mn ₃ O ₄ nanotube ⁵⁵	441.4 $F \cdot g^{-1}$	$2.0\ mV{\cdot}s^{-1}$	-0.2-0.4	-	$93/1000/5 \text{ mV} \cdot \text{s}^{-1}$	0.5 M ^a	-
ZnO/MnO ₂ nanowire/ nanosheet ⁵⁶	$275 \ \text{F}{\cdot}\text{g}^{-1}$	2.0 $A \cdot g^{-1}$	0-0.8	35	97/2000/10 A·g ⁻¹	1 M ^a	24/850
$ZnMn_2O_4/carbon^{57}$	$105 \ F \cdot g^{-1}$	$0.3 \text{ A} \cdot \text{g}^{-1}$	-1 to -0.3	72	97/5000/0.3 – 1 A·g ⁻¹ (variable)	6 M ^d	_
ZnO/rGO nanoflower ⁵⁸	$203 \text{ F} \cdot \text{g}^{-1}$	$1.0 \text{ A} \cdot \text{g}^{-1}$	-1.0-0	45	98/10,000/20 A·g ⁻¹	3.5 M ^d	-
$ZnMn_2O_4/C^{59}$	589 F·g ⁻¹	$1.0 \text{ A} \cdot \text{g}^{-1}$	0-1.2	47	$98/2000/10 \text{ A} \cdot \text{g}^{-1}$	1 M^{a}	-
ZnO-Au-NiO ²⁴	$4.1 \text{ F} \cdot \text{cm}^{-2}$	$5.0 \text{ mA} \cdot \text{cm}^{-2}$	0-0.5	~100	$80/4000/30 \text{ mA}\cdot\text{cm}^{-2}$	1 M^d	-
ZnO-/coral-like MnO2 ¹⁵	221 $F \cdot g^{-1}$	$0.5 \text{ A} \cdot \text{g}^{-1}$	0-0.8	55	$86/3000/5 \ A \cdot g^{-1}$	1 M ^a	-
MnO ₂ -shell/ZnO- nanowire/carbon fabric ¹⁸	$0.2 \text{ F} \cdot \text{cm}^{-2}$	$5.0 \text{ mA} \cdot \text{cm}^{-2}$	0-1	50	89/3000/5.0 mA·cm ⁻²	0.5 M ^a	16/27,000
ZnO/MnO Nanoflowers (present work)	556	$1.0 \text{ A} \cdot \text{g}^{-1}$	0-0.9	60	96/10,000 /1.0 A·g ⁻¹	1 M ^a	16/225

Table 2. Comparison of Specific Capacities Reported to Date with Those in the Present Study

^aNa₂SO₄. ^bPVA/LiCl gel. ^cPMMA–PC-LiClO4 gel. ^dKOH.



Figure 8. (a) Nyquist plots and (b) capacitance retention for long-term cycling performance of ZnO and ZnO/MnO_x NF electrodes. The first and last three GCD cycles of the ZnO/MnO_x NF-optimized electrode are magnified in the inset. Here, Z', Z'', R_s , R_{cv} , C, and Z_W denote the real impedance, imaginary impedance, resistance of the solution (electrolyte/electrode), charge-transfer resistance of electrochemical reactions, double-layer capacitance, and Warburg impedance, respectively.

when the potential was reversed. This indicates the excellent pseudocapacitance characteristics of the electrode, resulting from the MnO_x coating on the ZnO NF petals. The Columbic efficiency (CE) of the ZnO/MnO_x NFs was better than that of

the pure ZnO NFs. The Columbic efficiencies of the ZnO NFs were 77%, 80%, and 78% for the potential windows of 0.5, 0.7, and 0.9 V, respectively (Figure 6d). The Columbic efficiency increased noticeably to 91%, 88%, and 89% in the potential

windows of 0.5, 0.7, and 0.9 V, respectively, for the ZnO/ MnO_r NFs (Figure 7d). The GCD tests for the optimized ZnO/MnO_r NFs revealed the excellent charge/discharge ability of the electrode and indicated that the ZnO/MnO_x NFs presented higher capacitance than the pristine ZnO NFoptimized electrode (Figure 6e). The capacitances of the optimized ZnO/MnO_x NF supercapacitor electrode in the potential windows of 0-0.5, 0-0.7, and 0-0.9 V, as calculated from the galvanostatic discharge curves, were 394, 458, and 556 $F \cdot g^{-1}$, respectively, at the current density of 1 $A \cdot g^{-1}$. Moreover, the optimized ZnO/MnO_x NF electrode also exhibited excellent current rate capability, and its capacitance retention exceeded 60% when the current rate density was increased to 5 $A \cdot g^{-1}$ in the potential windows of 0–0.5, 0–0.7, and 0-0.9 V. It should be noted that at a high current rate the Faradaic reaction is expedited, which slows the penetration of the electrolyte ions to the active sites and enhances the formation of the electrostatic charge layer, reducing the total capacitance. Thus, the optimized electrode demonstrates significant potential as a supercapacitor electrode for highcurrent and high-power applications. The observed capacitance of the ZnO/MnO_x NFs exceeded those recently reported in the literature (Table 2) and is highly promising. The Ragone plot in Figure 7f shows the energy density of the supercapacitor cell as a function of the power density. High and low energy densities of 16 and 11.2 $Wh \cdot kg^{-1}$ were obtained at the power densities of 225 and 1125 $W \cdot kg^{-1}$, respectively, in the potential window of 0-0.9 V.

The EIS spectra of the ZnO and ZnO/MnO_x NF electrodes were acquired to examine the effects of the MnO_x decoration on the thin petals or nanosheets of the ZnO NFs. Figure 8a presents the Nyquist plots of the ZnO and ZnO/MnO_x NF electrodes, which consist of semicircles and straight lines. The semicircles in the Nyquist plots correspond to the highfrequency response; the first and second intercept with the real impedance axis (x axis) can be used to determine the resistance of the solution (electrolyte/electrode) (R_s) and charge-transfer resistance (R_{ct}) of the electrochemical reactions, respectively. The R_s of the ZnO NF-optimized electrode was slightly higher than that of the ZnO/MnO_x NF electrode. However, the R_{ct} of the optimized ZnO/MnO_x NF electrode was significantly lower than that of the optimized ZnO NF electrode, owing to the presence of MnO_x in the ZnO nanostructure. The lower R_{ct} of the optimized ZnO/MnO_x NF electrode is consistent with its superior electrochemical performance (Figures 5-7) compared with that of the ZnO NF supercapacitor electrode. The Nyquist plots of both electrodes were fitted using Randles equivalent circuits, and the fitting results are presented in Figure 8a using dashed lines. The R_s values of the ZnO/MnO_x and ZnO NF supercapacitor electrodes obtained by fitting the Nyquist plots were 12.6 and 14.2 Ω , respectively, and the corresponding $R_{\rm ct}$ values were 32.9 and 41.7 Ω .

Furthermore, the long-term electrochemical cycling performance of the ZnO and ZnO/MnO_x NF electrodes was investigated to confirm the effect of the MnO_x coating on ZnO; the results are displayed in Figure 8b. The electrochemical stability of the optimized ZnO/MnO_x NF electrode was superior to that of the ZnO NF electrode. During the GCD cycles, the long-term electrochemical performance of both electrodes was tested at a constant current density of 1 A· g^{-1} . The ZnO/MnO_x NF-optimized electrode presented excellent capacitance retention of more than 96% after

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10,000 GCD cycles. The first and last three GCD cycles for the ZnO/MnO_x NF electrodes are displayed in the inset of Figure 8b. The charge/discharge cycles depicted in the inset are almost identical, demonstrating the competent retention capability of the ZnO/MnO, NF electrode. However, the capacitance of the optimized ZnO NF electrode decreased rapidly owing to the chemical instability of ZnO. The optimized ZnO NF electrode displayed poor capacitance retention (~79% after 5000 GCD cycles) during long-term cycling. Evaluation of the long-term cycling performance of the ZnO NFs (sample C) (Figure S9) at a current rate of 5 $A \cdot g^{-1}$ showed a capacitance retention of 84% after 5,000 charge/ discharge cycles. The ZnO/MnO_x NFs provided a retention of 96.5% after 10,000 charge/discharge cycles. Thus, it could be inferred that although the bare ZnO nanostructures are easily synthesized their practical use is limited by their chemical instability. Notably, the shape of the CV curves of the ZnO/ MnO_x NFs is similar to that of electric double-layer capacitors (Figure 5d), while that of the ZnO NFs is not (Figure 5a). MnO_x adsorbs cations and incorporates protons efficiently, thereby promoting the reversible surface redox reaction.⁵¹ The electrochemical performance of the ZnO/MnO_x NFs is more stable than that of the ZnO NFs, indicating the positive influence of the synergetic effect between ZnO and MnO_x. As shown in Figure 8b, the hierarchical layered structure of MnO_x over the ZnO NFs improved the stability of the SC electrode. In addition, the binder-free ZnO NF provides better electrolytic accessibility and more rapid charge transfer capability. Removal of impurities provides enhanced electrical conductivity and hence mobility of the ions.^{47,52} The surface morphology of ZnO and the ZnO/MnO_x NFs after cycling was examined from the SEM images in Figure S8. The nanoflower structure of ZnO and ZnO/MnO_x NF remained intact even after thousands of charge-discharge cycles. The surface of ZnO NFs appeared to be roughened, which may be due to oxide formation. However, no evidence of structural changes or degradation was observed in Figure S8c and d. Hence, coating novel ZnO nanostructures with materials such as MnO_x or TiO₂ may be useful and very important for practical application as well as for synthesis.

CONCLUSIONS

ZnO/MnO_x NFs were prepared via a facile and cost-effective process that consisted of electrodeposition followed by CBD on Ni NC/Cu substrates. The heterostructured ZnO/MnO_r NFs could provide more electrochemical sites and faster electron transport than thin films. The combination of the morphology and heterostructure of the composite electrodes yielded ideal pseudocapacitive behavior in environmentally safe aqueous electrolytes in the operating voltage window of 0-0.9 V. The optimized electrode exhibited excellent electrochemical stability, and its capacitance retention after 10,000 cycles was 96%. Moreover, the optimized electrode delivered remarkable current rate capability, high energy density (16 Wh·kg⁻¹ at the power density of 225 W·kg⁻¹), and an excellent capacitance of 556 $F \cdot g^{-1}$ at a current density of 1 A $\cdot g^{-1}$. Thus, the prepared electrodes are potentially economical and promising choices for use in aqueous electrolytes for high-energy-density supercapacitors.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acssuschemeng.9b06796.

Surface morphology, cycling voltammetry, and long-term capacitance retention data of the fabricated films. (PDF)

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Notes

The authors declare no competing financial interest.

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