One-Step Hydrothermal Synthesis of Nitrogen-Doped Reduced Graphene Oxide/Hausmannite Manganese Oxide for Symmetric and Asymmetric Pseudocapacitors

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ABSTRACT: In this paper, the pseudocapacitive performance of nitrogen-doped and undoped reduced graphene oxide/tetragonal hausmannite nanohybrids (N-rGO/Mn3O4 and rGO/Mn3O4) synthesized using a one-pot hydrothermal method is reported. The nanohybrid electrode materials displayed exceptional electrochemical performance relative to their respective individual precursors (i.e., reduced graphene oxide (rGO), nitrogen-doped reduced graphene oxide (N-rGO), and tetragonal hausmannite (Mn3O4)) for symmetric pseudocapacitors. Among the two nanohybrids, N-rGO/Mn3O4 displayed greater performance with a high specific capacitance of 345 F g\(^{-1}\) at a current density of 0.1 A g\(^{-1}\), excellent specific energy of 12.0 Wh kg\(^{-1}\) (0.1 A g\(^{-1}\)), and a high power density of 22.5 kW kg\(^{-1}\) (10.0 A g\(^{-1}\)), while rGO/Mn3O4 demonstrated a high specific capacitance of 264 F g\(^{-1}\) (0.1 A g\(^{-1}\)) with specific energy and power densities of 9.2 Wh kg\(^{-1}\) (0.1 A g\(^{-1}\)) and 23.6 kW kg\(^{-1}\) (10.0 A g\(^{-1}\)), respectively. Furthermore, the N-rGO/Mn3O4 nanohybrid exhibited an impressive pseudocapacitive performance when fabricated in an asymmetric configuration, having a stable potential window of 2.0 V in 1.0 M Na2SO4 electrolyte. The nanohybrid showed excellent specific energy and power densities of 34.6 Wh kg\(^{-1}\) (0.1 A g\(^{-1}\)) and 14.01 kW kg\(^{-1}\) (10.0 A g\(^{-1}\)), respectively. These promising results provide a good substance for developing novel carbon-based metal oxide electrode materials in pseudocapacitor applications.

1. INTRODUCTION

Electrochemical energy storage devices have emerged as the key technological solution to the rising energy demand and the limited availability or harsh environmental impact of fossil fuels.\(^1\)\(^,\)\(^2\) Such energy storage devices should be able to deliver robust power and energy outputs while being able to still retain their stability and efficiency after long charge–discharge cycles. The inherent high efficiency of an electrochemical energy storage device and its capability to store the harnessed energy from renewable energy sources such as solar, wind, etc., has drawn much attention in the current energy research.\(^3\)\(^,\)\(^4\) Among the electrochemical energy storage devices, supercapacitors (SCs) have proved to possess such characteristics as described above and hence continue to receive much attention from the scientific research community.\(^5\) The primary goal for the choice of supercapacitors as a device of choice is to design and develop a new type of technology that surely surpasses and bridges the gap between batteries (famous for their high energy densities) and conventional capacitors (famous for their high power densities).\(^6\) Apart from the current trend of supercapacitors being used as a supportive energy storage device in renewable energy sources, these devices are also mostly used in a variety of applications such as hybrid electric vehicles (HEVs), portable electronic devices, and backup power memory.\(^7\) Furthermore, the charge storage mechanism in SCs is different from the one in batteries. There are three classes of SCs based on their charge storage mechanisms: all-carbon-based electrical double-layer capacitors (EDLCs), pseudocapacitors, and hybrid capacitors.\(^8\)\(^−\)\(^12\) The EDLCs can store energy by charge separation at the electrode/electrolyte interface, whereas the pseudocapacitors use electroactive metal oxide and/or conducting polymers to store energy by redox or Faradaic processes. It was seen that the hybrid capacitors incorporate both the Faradaic reactions (pseudocapacitance) and the non-Faradaic reactions (EDLCs).\(^8\)\(^−\)\(^12\)

The pseudocapacitor and the hybrid capacitor are reported to exhibit superior capacitance in comparison with the EDLC, with the hybrid capacitor ranking high. Nonetheless, it is documented that the physicochemical properties of the...
working-electrode materials affect the performance of supercapacitors. Nevertheless, one of the major shortcomings of the pseudocapacitive electrode materials as compared to counterpart electrode materials is their poor rate-capability as a result of poor conductivity. In an effort to develop a high capacitive supercapacitor, nanostructured carbon materials are incorporated with electroactive species such as metal oxides or conducting polymers to achieve improved electrochemical performance. The intensive use of the nanostructured carbon materials is owing to their exceptional properties, including a higher specific surface area of around 2000 m² g⁻¹, nontoxicity, good chemical stability, natural abundance, and excellent electronic conductivity. Among several carbon nanomaterials discovered and explored for energy storage applications in the manganese oxide family and has single black manganese dioxide with Mn3O4 lead to poor cycle reversibility. However, the poor electronic conductivity and manganese dissolution of Mn3O4 lead to poor cycle stability with respect to the rGO/Mn3O4 nanohybrid exhibiting excellent pseudocapacitive properties such as specific capacitance, rate performance, and cycle stability with respect to the rGO/Mn3O4 nanohybrid and their precursors.

The interest in using transition-metal oxides (TMOs) as electrode materials for SC applications has increased. Among TMOs, manganese oxides, MnOₓ, appeared to be the promising electrode material for pseudocapacitors because of their interesting properties, including cost-effectiveness, great theoretical specific capacitance, extraordinary theoretical surface area (≥1370 m² g⁻¹), and excellent electrochemical reversibility. The MnO₂ is one of the most stable oxides in the manganese oxide family and has single black manganese with controllable microstructures at room temperature. This makes it an ideal material for supercapacitors in terms of cost-effectiveness, high specific capacitance, and being environmentally friendly. However, the poor electronic conductivity and manganese dissolution of MnO₂ lead to poor cycle stability, which restricts its progress in SC applications. Therefore, it is essential to improve the electronic conductivity of MnO₂ by the addition of any conductive additives such as OLCs, CNTs, graphene, and rGO. Reported on a MnO₂ thin-film electrode material with a specific capacitance of 92 and 58 F g⁻¹ in aqueous electrolytes and organic electrolytes, respectively. However, the combination of MnO₂ with MWCNT (MnO₂/MWCNT composite) displayed a maximum specific capacitance of 330 F g⁻¹. In contrast, the MnO₂/graphene composite exhibited a specific capacitance of 175 F g⁻¹ while MnO₂ decorated with an onionlike carbon (OLC/MnO₂ nanohybrids) in a symmetric configuration exhibited a specific capacitance and maximum energy of 195 F g⁻¹ and 4.3 Wh kg⁻¹, respectively. The power density of this nanohybrid was reported to be 52 kW kg⁻¹. The OLC/MnO₂ nanohybrids also showed a maximum energy density of 19 Wh kg⁻¹ at 0.1 A g⁻¹ current density and a power density of 45 kW kg⁻¹ at 10 A g⁻¹ current density during an asymmetric configuration. The functionalization of graphitic carbon materials introduces lattice defects that improve the electronic and catalytic activity of the graphitic material, resulting in better interactions with the electrolytes and thus enhancing the wettability of the material. On the other hand, carbon-based materials doped with nitrogen, boron, phosphorus, and sulfur heteroatoms in different combinations result in the superior performance of energy storage devices. In this study, we have explored the facile synthetic process (one-pot synthesis) for tuning the electronic structure of rGO by introducing the N-atoms, followed by anchoring of the MnO₂ onto the surface of the N-rGO to form a nanohybrid with improved conductivity. The as-prepared N-rGO/MnO₂ nanohybrid exhibited excellent pseudocapacitive properties such as specific capacitance, rate performance, and cycle stability with respect to the rGO/MnO₂ nanohybrid and their precursors.

2. EXPERIMENTAL SECTION

2.1. Preparation of Electrode Materials

2.1.1. Synthesis of Graphene Oxide (GO). Graphene oxide was prepared using the exfoliation of graphite according to a modified Hummers’ method. Briefly, a graphite rod (6.15 mm (diameter) × 152 mm (long), 99.9995% (metal basis), AGKSP grade, ultra “F” purity) acquired from Alfa Aesar (a Johnson Matthey Company) was ground to a fine powder using a pestle and mortar, followed by filtering through a 210-micron sieve. The filtered graphite powder and 1.0 g of NaNO₃ (1:1 mass ratio) were weighed into a 250.0 mL beaker, and 50.0 mL of concentrated H₂SO₄ was gradually introduced to the mixed powder at 0 °C. After 15 min, a 30% H₂O₂ solution was added. The solution mixture was then stirred constantly for 1 h at 25 °C. The mixture was slowly transferred into a 400.0 mL beaker containing 200 mL of deionized water, and after 15 min, a 30% H₂O₂ solution was added. The reaction mixture was then stirred at constant stirring until the gas evolution ceased. The reaction mixture was then filtered, and the precipitate was washed repeatedly with 5% HCl solution and deionized water. Finally,
the powders were dried overnight at 60 °C in an oven to obtain the yellow-brown solid of GO.

2.1.2. Syntheses of N-rGO/Mn$_3$O$_4$ and rGO/Mn$_3$O$_4$ Nanohybrids and Other Precursurs. The preparation of N-rGO/Mn$_3$O$_4$ and rGO/Mn$_3$O$_4$ nanocomposites followed a facile one-pot hydrothermal reaction (see Scheme 1). For N-rGO/Mn$_3$O$_4$, GO (0.31 g) was dispersed in 600 mL of deionized water and ultrasonicated for 1 h. The solution was then transferred into a 1.0 L round-bottomed flask, and about 150 mL of an aqueous solution of 1 mg/mL KMnO$_4$ was added to the flask. Then, 3.0 mL of 25% NH$_3$ solution was added to the mixture under constant stirring, and subsequently, 3.0 mL of 99% hydrazine hydrate was slowly added to the reaction mixture, and ultimately the solution was refluxed for 3 h at 95 °C. The black color solution was then filtered, and the product was washed with a copious amount of water and ethanol and then dried overnight in an oven to afford N-rGO/Mn$_3$O$_4$. The synthesis of rGO/Mn$_3$O$_4$ followed the abovementioned process in the absence of NH$_3$. The synthesis of N-rGO and rGO followed similar conditions that were used in the abovementioned procedure, in the absence of KMnO$_4$ (N-rGO) and NH$_3$ (rGO). The synthesis of hausmannite Mn$_3$O$_4$ followed the above procedure in the absence of GO and NH$_3$.  

2.2. Microscopic and Spectroscopic Evaluation. The microscopic properties of the synthesized materials were probed using a scanning electron microscope (SEM; JSM-7500F, JEOL, Japan) fitted with energy-dispersive X-ray spectroscopy (EDS; for elemental analysis and mapping). The structural elucidation and elemental composition analyses were obtained using an X-ray diffractometer (XRD; Rigaku Ultima IV) equipped with Ni-filtered Cu Kα radiation (λ = 1.541841 Å) operating a copper tube at 30 kV and 40 mA. A Raman WITec Confocal Microscope (WITec α 300, Germany) with a laser wavelength of 532 nm, a laser power of 4 mW, and a spectral acquisition time of 120 s and an X-ray photoelectron spectroscope (XPS; PHI 5000 Versaprobe-Scanning ESCA Microprobe Instrument, ESCA) were used.

2.3. Electrode Fabrication. Fabrication of the electrodes was done by mixing the active materials (80%) with carbon black (15%) and poly(vinylidene fluoride) (5%) using a pestle and mortar, followed by the addition of anhydrous N-methyl-2-pyrrolidone (NMP) to make a homogeneous paste. Poly(vinylidene fluoride) and carbon black functioned as the binder and conductive materials, respectively. Nickel foam pretreated with 1.0 M HCl, washed with deionized water, and dried under vacuum was used as a current collector. All of the prepared electrodes were dried at 80 °C overnight in a vacuum oven. The electrochemical cell was constructed in a two-electrode system using a Swagelok cell with electrodes assembled in respective symmetric and asymmetric configurations. A porous glass fiber (Whatman Grade GF/D glass microfiber filters, Sigma-Aldrich) and 1.0 M Na$_2$SO$_4$ solution were employed as the separator and electrolyte, respectively.

2.4. Electrochemical Evaluation. A Bio-Logic VMP 300 potentiostat/galvanostat (EC-Lab v10.40 software) was used for the electrochemical evaluations of the synthesized electrode materials. Cyclic voltammetry (CV) analyses were recorded at various scan rates between 2 and 100 mV s$^{-1}$ in a potential range of 0 to 1.0 V. Galvanostatic charge–discharge (GCD) analyses were recorded from various current densities between 0.1 and 10 A g$^{-1}$. Electrode resistance properties were probed using the electrochemical impedance spectroscopy (EIS) technique employing a frequency range from 0.1 Hz to 100 kHz under an open-circuit potential, and the data were fitted using the Z-fit tool. The stability evaluation of the electrodes was obtained via voltage holding for 10 h (times 5) at 1.1 V with subsequent GCD analysis between a potential window of 0.0 and 1.1 V (at 2.0 A g$^{-1}$). The electrochemical performance parameters (i.e., specific capacitance (C$_{sp}$), specific maximum power density (P$_{max}$), and specific energy density (E$_{sp}$)) of the electrode materials were derived from GCD curves by following eqs 1−5.$^{31}$

\[
C(F) = \frac{i}{\Delta V/\Delta t} \quad (1)
\]

\[
C_{sp}(F/g) = \frac{4 \cdot C}{m} \quad (2)
\]

\[
P_{max}(10^3 W/kg) = \frac{V^2}{4mR} \quad (3)
\]

\[
E\left(\frac{1}{3.6}\right) Wh/kg = \frac{CV^2}{2m} \quad (4)
\]

\[
R_s(\Omega) = \frac{\Delta V_{IR}}{2i} \quad (5)
\]

where C represents the cell capacitance in Farads (F), $i$ represents the applied current in amperes (A), $V$ represents the potential in volts (V), $t$ represents the time in seconds (s), $m$ is the total mass of the electrodes in grams (g), $R_s$ represents the equivalent series resistance (ESR) in ohms (Ω) determined from the IR drop, and $\Delta V_{IR}$ represents the drop in voltage of the first two points on the discharge curve.

The evaluation of the electrochemical performance in an asymmetric configuration was achieved using activated carbon (AC) as the negative electrode and the N-rGO/Mn$_3$O$_4$ nanohybrid as the positive electrode. The mass balancing of the individual electrodes using a three-electrode system (i.e., $m_{P}/m_{S} = 0.34$), as an essential step in the optimization of the cell voltage to maintain equal charges, was achieved using eq 6

\[
m_s = \frac{m_{P} \times \Delta E_{r}}{\Delta E_{p}} \quad (6)
\]

where $m_s$ and $m_{P}$ represent the mass, $C_{sp}$ and $C_{sp}$ represent the specific capacitance, and $\Delta E_{r}$ and $\Delta E_{p}$ represent the potential window of the individual positive and negative electrode, respectively.

3. RESULTS AND DISCUSSION

3.1. Formation Mechanism: One-Pot Synthesis of the N-rGO/Mn$_3$O$_4$ Nanohybrid. Scheme 1 demonstrates the formation mechanism of the N-rGO/Mn$_3$O$_4$ nanohybrid. The presence of NH$_3$ facilitates the doping of N-atoms on the carbon material, while the KMnO$_4$ acts as the precursor of manganese oxide to form Mn$_3$O$_4$ nanoparticles. The N-doping and the reduction of both Mn$^{7+}$ to Mn$^{3+}$ and GO to rGO are done in situ via the presence of hydrazine, which is a strong reducing agent. The formation of rGO/Mn$_3$O$_4$ took place using a similar route but in the absence of NH$_3$.

3.2. Scanning Electron Microscopy (SEM) Analysis. To understand the surface morphology of the synthesized materials, SEM analysis was performed, as shown in Figure 1, which depicts microscopic images of (a) N-rGO/Mn$_3$O$_4$, (b) rGO/Mn$_3$O$_4$, and (c) N-rGO.
The crystalline Mn$_3$O$_4$, the wrinkled rGO, and the wrinkled and chaotically flaky N-rGO can be observed in the images of Figure 1f rGO/Mn$_3$O$_4$ and (g) N-rGO/Mn$_3$O$_4$. These traits can be correlated back to those of the individual N-rGO, rGO, and Mn$_3$O$_4$ in Figure 1c−e, respectively, indicating a successful decoration of Mn$_3$O$_4$ nanoparticles on rGO and N-rGO. The introduction of nitrogen onto the structure of rGO resulted in the chaotic flaky morphology of N-rGO.

### 3.3. XRD, Raman, and EDX Analyses

The structural and chemical constituency of the as-prepared nanomaterials was investigated using the XRD, Raman, and EDX characterization techniques. Diffraction patterns of graphite, GO, rGO, and N-rGO in Figure 2a show a graphitic peak at 2θ = 26.43° corresponding to the (002) diffraction plane with an interlayer spacing of about 3.37 Å. The same peak can be observed from the spectra of N-rGO/Mn$_3$O$_4$ and rGO/Mn$_3$O$_4$ in Figure 2b. The d-spacing value is approximate to that reported in the literature of 3.35 Å for graphitic carbon with oriented layers.$^{32-34}$ The diffraction pattern of GO shows a sharp peak at 2θ = 11.59° that correlates to the (002) diffraction plane with an interplanar spacing of 5.50 Å, as well as a miniature graphitic peak centered at about 2θ = 26°, which confirms the successful oxidation of graphite.$^{35,36}$ The increase in interlayer spacing from graphite to GO confirms the expansion of the graphitic stack due to the presence of oxygen functionalities over graphene layers.$^{37}$ The successful reduction of GO is confirmed by the disappearance of the GO characteristic diffraction peak at 2θ = 11.59° and the appearance of the broadened (002) diffraction peak centered at about 2θ = 26° for rGO, N-rGO, rGO/Mn$_3$O$_4$, and N-rGO/Mn$_3$O$_4$. The broadening of the peak at about 26° (between 19 and 25°) for rGO, N-rGO, rGO/Mn$_3$O$_4$, and N-rGO/Mn$_3$O$_4$ may be ascribed to the presence of disordered rGO layers.$^{39}$ Figure 2b illustrates the XRD spectra of N-rGO/Mn$_3$O$_4$, rGO/Mn$_3$O$_4$, and Mn$_3$O$_4$ overlaid with the standard diffraction spectra of the graphitic material (RRUFF ID: R090047) and hausmannite Mn$_3$O$_4$ (RRUFF ID: R110179). The peaks from the Mn$_3$O$_4$ spectrum can also be observed in the spectra of the nanohybrids, all of which correspond to the diffraction pattern of the hausmannite Mn$_3$O$_4$ standard. These peaks, observed at 14.19, 17.94, 28.95, 32.32, 36.05, 38.14, 44.30, 50.79, 58.40, 59.84, and 64.57°, are characteristic of the (001), (101), (112), (103), (211), (004), (220), (105), (321), (224), and (400) diffraction planes of body-centered tetragonal hausmannite Mn$_3$O$_4$, respectively.$^{40}$ The planes show interlayer spacings of 6.20, 4.92, 3.09, 2.77, 2.49, 2.36, 2.04, 1.79, 1.58, 1.54, and 1.44 Å, respectively. On average, the interlayer spacing of the samples is calculated at 3.37, 5.50, 3.52, and 5.53 Å for graphite, GO, rGO, and N-rGO in Figure 2a and at 2.81, 2.80, and 2.75 Å for N-rGO/Mn$_3$O$_4$, rGO/Mn$_3$O$_4$, and Mn$_3$O$_4$ in Figure 2b, respectively. This shows the variation in the interlayer spacing due to the respective treatments used during material preparation. The average in-plane crystallite size of the samples is observed to have decreased from graphite (29.36 nm) to 8.53, 5.15, and 5.57 nm for GO, rGO, and N-rGO, respectively, which is similar to the trends observed in the literature.$^{37,41}$ Conversely, the average crystallite sizes of the rGO/Mn$_3$O$_4$ and N-rGO/Mn$_3$O$_4$ nanohybrids of 12.44 and 15.16 nm, respectively, show a significant decrease with respect to the 24.64 nm for Mn$_3$O$_4$, whereas they show a significant increase with respect to the other carbonaceous precursor material.

The Raman spectra in Figure 2c show characteristic D-mode and G-mode bands at 1349 and 1600 cm$^{-1}$, respectively, for both rGO/Mn$_3$O$_4$ and N-rGO/Mn$_3$O$_4$ nanohybrids, indicating the defected carbon backbone. The D and G band ratios ($I_D/I_G$) of the nanohybrids are 1.68 and 1.75, respectively, which did not change significantly from the 1.79, 1.52, and 1.45 of GO, rGO, and N-rGO, respectively. A slight increase in the
ratio was observed from rGO/Mn$_3$O$_4$ to N-rGO/Mn$_3$O$_4$, which could be attributed to the increase in the defects brought on by doping nitrogen, added to the growth of hausmannite manganese oxide onto the conjugated carbon framework. The presence of crystalline Mn$_3$O$_4$ nanoparticles in the nanohybrids is confirmed by the dominant peak at 460 cm$^{-1}$ and the small peaks between 250 and 400 cm$^{-1}$, which are also seen on the overlaid Mn$_3$O$_4$ spectrum. The N-rGO/Mn$_3$O$_4$ and rGO/Mn$_3$O$_4$ nanocomposites are seen to have retained the structural integrity of both rGO and Mn$_3$O$_4$. The XRD and Raman results further affirm the SEM image results of the successful integration of Mn$_3$O$_4$ with rGO and N-rGO, respectively.

Figure 2d shows the EDX spectra of graphite, GO, rGO, N-rGO, N-rGO/Mn$_3$O$_4$, rGO/Mn$_3$O$_4$, and Mn$_3$O$_4$. A dominant peak characteristic of carbon is observed at 0.25 keV in the EDX spectra, which is due to the carbon coating used and the carbon of the graphitic materials synthesized. An oxygen peak is observed at about 0.52 keV in the spectra of GO, rGO, N-rGO, N-rGO/Mn$_3$O$_4$, rGO/Mn$_3$O$_4$, and Mn$_3$O$_4$, signaling the...
presence of oxygen in the samples. A small peak signaling the presence of sulfur in the spectrum of GO comes from using sulfuric acid in the synthesis of GO using the modified Hummers method and is washed away by succeeding procedures. The peaks characteristic of manganese are observed at 5.8 and 6.4 keV in the spectra of N-rGO/Mn₃O₄, rGO/Mn₃O₄, and Mn₃O₄. The miniaturized intensities of the peaks of oxygen and manganese in the spectra of N-rGO/Mn₃O₄ are possibly due to the use of a lot of the carbon coating, which adds to the intensity of the graphene carbon. The presence of nitrogen was confirmed by comparing the deconvoluted spectra of N-rGO and N-rGO/Mn₃O₄ with that of rGO in Figure 2e. A peak of nitrogen can be observed at 0.3 keV in the spectra of N-rGO and N-rGO/Mn₃O₄ which is eclipsed by the peak of carbon. This particular peak is absent in the spectrum of rGO. The successful integration of hausmannite Mn₃O₄ onto N-rGO is further supported by the spectrum of rGO. The presence of the pyridinic and pyrrolic nitrogen in the core structure of graphene improves its electrical and electrochemical performance during the electrochemical process. The narrow oxygen peak (O 1s) was deconvoluted into four peaks, as observed in Figure 4d. The peak observed at 529.8 eV is typical of the bonding configuration of O–Mn atoms in hausmannite Mn₃O₄, while the peak at 531 eV demonstrates the presence of the C==O functional group, and the peak at 532.9 eV reveals the presence of C–O–C/C–OH bonding configurations in rGO.56,51 As previously reported,52,53 the peak observed at 530.8 eV is attributed to the formation of a Mn–O–C bond. It was shown that Mn₃O₄ binds with graphene through a bond formed between the manganese ion and oxygen-containing functional groups on the surface of graphene. Formation of the Mn–O–C bond further reduces the oxygen-containing functional groups on rGO by substitution of manganese on C==O and C–OH/C–O–C groups. Figure 4f demonstrates two peaks of Mn 2p at 641.3 and 653.1 eV, which are characteristic of Mn 2p₁/₂ and Mn 2p₃/₂, respectively. The Mn 2p spectrum shows a splitting width of 11.8 eV, which is a validation that the prominent manganese oxide in the nanohybrid is the Mn₃O₄.50

3.5. Electrochemical Evaluations. 3.5.1. Performance of the N-rGO/Mn₃O₄ Nanohybrid in a Symmetric Configuration. Figure 5a illustrates the cyclic voltammograms of N-rGO/Mn₃O₄, rGO/Mn₃O₄, rGO, N-rGO, and Mn₃O₄ at a scan rate of 5 mV s⁻¹. The cyclic voltammograms of the N-rGO/Mn₃O₄ and rGO/Mn₃O₄ nanohybrids exhibited a quasi-rectangular shape due to the Faradaic charge and pseudocapacitive storage mechanisms of the carbon material and metal oxide, respectively, in the nanohybrid electrode materials. Greater response in current and charge separation was observed from the cyclic voltammograms of the N-rGO/Mn₃O₄ nanohybrid, compared to the rGO/Mn₃O₄ nanohybrid and the precursor materials. The integration of Mn₃O₄ and N-rGO resulted in a synergistic effect on the N-rGO/Mn₃O₄ nanohybrid, enhancing its electrochemical performance as compared to the other synthesized electrode materials in this study. Furthermore, the results show the enhanced electrochemical performance arising from doping nitrogen on the nanohybrid. Figure 5b shows the cyclic voltammograms of N-rGO/Mn₃O₄ at various scan rates ranging from 2 to 100 mV s⁻¹ in a potential window range of 0–1.0 V. As in Figure 5a, the cyclic voltammograms illustrated in Figure 5b show the ideal quasi-rectangular shape. The deviation from the perfect rectangular shapes arises from the electrode material’s internal resistance that impedes charge mobility within its porous structure.54 This is demonstrated by the steady change of the curves to a sharp climax that is observed when they approach 1.0 V and the scan rate decreases.

Figure 5c compares the GCD curves of N-rGO/Mn₃O₄, rGO/Mn₃O₄, N-rGO, rGO, and Mn₃O₄ in an aqueous 1 M Na₂SO₄ solution at a current density of 0.1 A/g and a cell voltage range of 0–1.0 V. The fairly symmetrical curves of N-rGO/Mn₃O₄ and rGO/Mn₃O₄ showed excellent capacitive performance and electrochemical reversibility, with N-rGO/Mn₃O₄
Mn$_3$O$_4$ showing superior performance that compliments the CV results. Similar outcomes can be seen in Figure 5d, which illustrates an extensive GCD investigation of N-rGO/Mn$_3$O$_4$ at various current densities ranging between 0.1 and 10.0 A g$^{-1}$. The nanohybrid material showed excellent electrochemical activity at 0.1 A g$^{-1}$, but it decreased as the current density increased to 10.0 A g$^{-1}$. This correlates to a decrease in the specific capacitance as current density increases, as shown in Figure 6a, which shows the dependence of $C_p$ on current density for N-rGO/Mn$_3$O$_4$, rGO/Mn$_3$O$_4$, N-rGO, rGO, and Mn$_3$O$_4$. Table 1 demonstrates the inverse relationship of current density with capacitance and energy density and its directly proportional relationship with power density. Using the GCD data obtained from Figure 5c,d and eqs 1–4, the N-rGO/Mn$_3$O$_4$ nanohybrid electrode material was found to possess a maximum specific capacitance ($C_{sp}$) of 345 F g$^{-1}$ and a specific energy density ($E_{sp}$) of 12.0 Wh kg$^{-1}$ at 0.1 A g$^{-1}$, which is higher than those for rGO/Mn$_3$O$_4$ at 268 F g$^{-1}$ and 9.2 Wh kg$^{-1}$, respectively. The improved specific capacitance of N-rGO/Mn$_3$O$_4$ is attributed to the introduction of the heteroatom (N-doping), which induces surface defects and thus decreases the charge transfer resistance through better accessibility of the electrolyte to the active material. However, the rGO/Mn$_3$O$_4$ nanohybrid showed a slightly higher maximum specific power density ($P_{max}$) of 23.6 kW kg$^{-1}$ at 10.0 A g$^{-1}$ compared to the N-rGO/Mn$_3$O$_4$ nanohybrid (22.5 kW kg$^{-1}$). The Ragone plot in Figure 6b illustrates the specific energy and power densities of N-rGO/Mn$_3$O$_4$, rGO/Mn$_3$O$_4$, N-rGO, rGO, and Mn$_3$O$_4$ at varying current densities (0.1, 0.3, 0.5, 1.0, 2.0, 5.0, and 10.0 A g$^{-1}$). In comparison to the literature on Mn$_3$O$_4$-based aqueous ECs (Table 2), the proficient maximum specific capacitance and higher power-output results of the N-rGO/Mn$_3$O$_4$ and rGO/Mn$_3$O$_4$ nanohybrid electrode materials put them at an advantage of finding application in systems requiring high energy and power outputs. The N-rGO/Mn$_3$O$_4$ nanohybrid electrode has demonstrated the effect of doping nitrogen onto the carbon support (rGO), the synergistic benefit of integrating N-rGO

Figure 4. XPS survey spectra of (a) N-rGO/Mn$_3$O$_4$ and a narrow spectra of (b) C 1s, (c) N 1s, (d) O 1s, and (e) Mn 2p.
and Mn₃O₄, and its competence as electrode material in an symmetric capacitive system (Table 3).

EIS was employed as a valuable technique for better understanding the impedance properties of the synthesized electrode materials in terms of their resistivity and capacitive behaviors. Figure 6c shows the Nyquist plots comparing N-rGO/Mn₃O₄, rGO/Mn₃O₄, N-rGO, rGO, and Mn₃O₄ in a frequency range from 0.1 Hz to 100 kHz with an open-circuit potential. Extrapolating the vertical portion of the Nyquist plot to the real axis of each curve gives the equivalent distributed resistance, which is comprised of both the ionic resistance within the porous electrode material (i.e., the RC semicircle) and the equivalent series resistance (ESR). The resistance from the bulk solution (ESR), which is due to the electrolyte solution, is the x-intercept (i.e., the beginning of the semicircle). The N-rGO/Mn₃O₄ and rGO/Mn₃O₄ nano-hybrids showed ESR values of 0.53 and 0.68, respectively, while N-rGO, rGO, and Mn₃O₄ electrode materials displayed the ESR values of 0.35, 0.36, and 0.90 Ω, respectively. The charge transfer resistance (Rct) values for N-rGO (0.45 Ω) and rGO (0.52 Ω) were found to be much smaller than that of the Mn₃O₄ (4.35 Ω). This indicates good charge transfer mobility within the electronic structure of these carbon materials with the ions in the solution as compared to Mn₃O₄. The N-rGO/Mn₃O₄ (1.89 Ω) and rGO/Mn₃O₄ (2.10 Ω) nanohybrids also displayed smaller charge transfer resistance compared to the Mn₃O₄, indicating improved charge mobility due to the synergistic effect between the N-rGO and/or rGO with the Mn₃O₄. The improved electronic properties of N-rGO are induced by the N-doping as compared to the rGO, and a similar trend is witnessed between the N-rGO/Mn₃O₄ in relation to the rGO/Mn₃O₄ nanocomposite. This observation justifies the notion of enhancing the electrochemical properties of the electrode material by doping nitrogen into the structure of the carbon support. This is supported by previous work conducted on nitrogen-doped carbon materials, indicating lower resistance observed from such electrode materials.60−63

In principle, adequate nitrogen-doping surface modification enhances the wetting of the electrode by the electrolyte,64−66 thus minimizing the interfacial charge transfer resistance.67

The electrochemical stability of the N-rGO/Mn₃O₄ nanohybrid was probed using voltage holding, GCD, and EIS techniques. Figure 7a illustrates the comparative GCD curves after repetitive floating five times for 10 h each interval, and Figure 7b shows the continuous GCD curve after voltage floating for 20 h at a current density of 2.0 A g⁻¹. The nanohybrid electrode material demonstrated outstanding electrochemical stability when cycled under voltage holding for over 50 h, with over 95% capacitance retention, as observed in Figure 7c, which shows the capacitance retention over time. Figure 7d shows the Nyquist plots of before and after voltage holding, while the inset shows a closeup view of the high-frequency region of the two plots.
3.5.2. Performance of the N-rGO/Mn₃O₄ Nanohybrid in an Asymmetric Configuration. An asymmetric pseudocapacitive system was set up to probe the N-rGO/Mn₃O₄ nanohybrid electrode material's energy density. While the high power density (and hence the fast charge–discharge rate) primarily influences the performance of SCs, improving the

Figure 6. (a) Cₛ p vs current density and (b) Ragone plot (at various current densities: 0.1–10.0 A/g). (c) Nyquist plots of N-rGO/Mn₃O₄, rGO/Mn₃O₄, N-rGO, rGO, and Mn₃O₄. Inset in (c): Randles equivalent circuit used to fit the data; Rₛ, R_ct, CPE, and Z_w are electrolyte resistance, charge transfer resistance, pseudocapacitance, and Warburg impedance, respectively.

Table 1. Comparison of the Electrochemical Performance of the Synthesized Nanohybrids and Their Precursors as Electrode Materials for SC Applications

| electrode              | Cₛ p (F g⁻¹) 0.1 A g⁻¹ | Cₛ p (F g⁻¹) 10.0 A g⁻¹ | Eₛ p (Wh kg⁻¹) 0.1 A g⁻¹ | Eₛ p (Wh kg⁻¹) 10.0 A g⁻¹ | Pₛ max (kW kg⁻¹) 0.1 A g⁻¹ | Pₛ max (kW kg⁻¹) 10.0 A g⁻¹ |
|------------------------|--------------------------|--------------------------|--------------------------|--------------------------|-----------------------------|-----------------------------|
| N-rGO/Mn₃O₄            | 345                      | 123                      | 12                       | 3.8                      | 6.47                        | 22.5                        |
| rGO/Mn₃O₄              | 268                      | 83                       | 9.2                      | 2.9                      | 6.32                        | 23.6                        |
| N-rGO                 | 70                       | 28                       | 2.5                      | 1.0                      | 1.96                        | 15.4                        |
| rGO                    | 60                       | 18                       | 2.0                      | 0.4                      | 2.5                         | 17.0                        |
| Mn₃O₄                 | 95                       | 38                       | 3.3                      | 1.3                      | 0.54                        | 12.9                        |

Table 2. Comparison of the Electrochemical Performance of Mn₃O₄-based Aqueous Symmetric Electrochemical Capacitors from the Literature

| electrode              | electrolyte              | Vₘₚ (V) | Cₛ p (F g⁻¹) | Eₛ p (Wh kg⁻¹) | Pₛ max (kW kg⁻¹) | refs |
|------------------------|--------------------------|---------|--------------|----------------|------------------|------|
| N-rGO/Mn₃O₄            | 1.0 M Na₂SO₄             | 1.0     | 345          | 12             | 22.5             | this work |
| rGO/Mn₃O₄              | 1.0 M Na₂SO₄             | 1.0     | 268          | 9.2            | 23.6             | this work |
| N-rGO/Mn₃O₄            | 1.0 M Na₂SO₄             | 1.0     | 288          | 9.2            | 23.6             | this work |
| Mn₃O₄@ODC              | 1.0 M NaOH               | 1.0     | 130          | 4.7            | 55               | 55   |
| HNCXs/Mn₃O₄            | 1.0 M Li₃SO₄, 1 M Li₂SO₄ | 1.8     | 248          | 27.8           | 4.5              | 56   |
| Mn₃O₄/PANI/graphene    | 1.0 M Na₂SO₄             | 1.0     | 1240         | 29.4           | 0.9              | 57   |
| NPCM/Mn₃O₄             | 1.0 M Na₂SO₄             | 1.6     | 384          | 16.5           | 0.2074           | 58   |
| Mn₃O₄/MnS              | 2.0 M KOH                | 0.6     | 744          | 16.5           | 12.9             | 59   |
The energy density of SCs is of great significance as it puts it at an advantage to be comparable to LIB application. This aspect can help curb the lag of conventional capacitors to batteries.

Figure 8a compares the CV curves of AC (between −1.0 and 0 V vs Ag/AgCl) and that of the N-rGO/Mn3O4 nanohybrid (0–1.0 V vs Ag/AgCl) at a scan rate of 5 mV s⁻¹ in aqueous 1 M Na2SO4. Both curves show acceptable electrochemical stability from which an asymmetric capacitive system capable of reaching a cell voltage of up to 2.0 V in an aqueous electrolyte can be devised. Figure 8b shows cyclic voltammograms of the asymmetric system at varying potential windows (1.4, 1.8, and 2.0 V) of the N-rGO/Mn3O4 asymmetric device at a scan rate of 5 mV s⁻¹ in 1 M Na2SO4. The CV curves demonstrated the ideal quasi-rectangular shape, which suggests impressive electrochemical activity even at the 2.0 V cell potential. Figure 8c depicts the GCD curves of the

| electrode           | electrolyte     | V_max (V) | C_sp (F g⁻¹) | E_sp (Wh kg⁻¹) | P_max (kW kg⁻¹) | refs   |
|---------------------|-----------------|-----------|--------------|----------------|----------------|--------|
| N-rGO/Mn3O4         | 1.0 M Na2SO4    | 2.0       | 34.6         | 14.01          | this work      |
| HNCCs/Mn3O4         | 1.0 M Li2SO4    | 2.2       | 54.5         | 44.5           | 5.6            | 60     |
| NiCo-LDH/Mn3O4      | KOH/PVA         | 1.7       | 57.03        | 9.7            | 68              |
| Mn3O4@NPC           | PVA-Na2SO4      | 2.6       | 76.96        | 1.30           | 69              |
| Mn3O4/TB/NHPC       | 1.0 M Na2SO4    | 1.8       | 78.3         | 34.7           | 70              |
| Mn3O4/rGO           | 1.0 M Na2SO4    | 0.5       | 351          | 36.76          | 71              |
| CNT/Mn3O4           | 1.0 M Na2SO4    | 1.8       | 135.2        | 37.0           | 72              |
| Mn3O4@NiCo3O4@NiO   | PVA/KOH         | 1.6       | 216          | 76.8           | 0.80            | 73     |
| AC/polyaniline/Mn3O4| 6 M KOH         | 1.2       | 33.8         | 6.1            | 74              |
| Mn3O4/rGO           | 1 M Na2SO4      |           | 31.9         | 0.50           | 75              |
| MnO2/Mn3O4          | 1 M Na2SO4      | 1.6       | 198.6        | 234            | 76              |
| Ti3C2/Mn3O4         | 6 M KOH         | 1.5       | 78.9**       | 28.3           | 2.29            | 77     |
| Mn3O4/Ni(OH)2       | 1 M KOH         | 1.6       | 43           | 15.3           | 3.2             | 78     |
| Mn3O4/PCM           | 3 M KOH         | 1.4       | 110.8        | 27.13          | 4.67            | 79     |

*Key: Specific gravimetric capacity (*C g⁻¹, **mAh g⁻¹).*

Figure 7. (a) GCD curves at various voltage holding times (0–50 h). (b) Continuous GCD curves after voltage holding for 20 h. (c) Capacitance retention of the electrode material at a current density of 2.0 A g⁻¹, and (d) Nyquist plot (before and after voltage holding) of N-rGO/Mn3O4 in aqueous 1.0 M Na2SO4 (Inset: closeup view of the high-frequency region).
asymmetric system at current densities ranging from 0.1 to 10 A g⁻¹. The asymmetric device showed excellent charge and discharge symmetry, indicating the enhanced electrochemical reversibility and capacitive performance of the system even at a maximum high cell potential of 2.0 V. The Ragone plot shown in Figure 8d demonstrates the asymmetric device as possessing an excellent maximum energy density of ca. 34.6 Wh kg⁻¹ at a current density of 0.1 A g⁻¹ and a maximum power density of 14.01 kW kg⁻¹ at 10 A g⁻¹. These outstanding results are observed to be comparable to previously reported literature on asymmetric ECs, as outlined in Table 2.

4. CONCLUSIONS
This study sought to investigate the electrochemical performance of the one-step synthesized nitrogen-doped reduced graphene oxide/haussmannite manganese oxide (N-rGO/Mn₃O₄) nanohybrid, its application as a pseudocapacitor electrode material in symmetric and asymmetric devices, and the effects of doping nitrogen on the reduced graphene oxide (rGO)-based carbon support. The N-rGO/Mn₃O₄ and rGO/Mn₃O₄ nanohybrids showed exceptional pseudocapacitive behavior in relation to the individual precursor materials (i.e., rGO, N-rGO, and Mn₃O₄). The N-rGO/Mn₃O₄ electrode material demonstrated a high specific capacitance of 345 F g⁻¹ at a current density of 0.1 A g⁻¹, excellent specific energy (12.0 Wh kg⁻¹), high power density (22.5 kW kg⁻¹), and excellent cycle stability in a symmetrical pseudocapacitive setup (see Figure 6), while the rGO/Mn₃O₄ nanohybrid displayed a high specific capacitance of 264 F g⁻¹ (0.1 A g⁻¹) with excellent specific energy and power densities of 9.2 Wh kg⁻¹ and 23.6 kW kg⁻¹, respectively. The N-rGO/Mn₃O₄ nanohybrid electrode material also displayed an impressive asymmetric pseudocapacitive performance with a stable potential window of 2.0 V in 1.0 M Na₂SO₄ electrolyte, a maximum energy density of 34.6 Wh kg⁻¹, and a maximum power density of 14.01 kW kg⁻¹. From the results obtained, this study has rationally demonstrated the excellent electrochemical performance and capacitive behavior of the N-rGO/Mn₃O₄ and rGO/Mn₃O₄ nanohybrids, which can be attributed to the synergistic effect of integrating N-rGO/rGO on Mn₃O₄.

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Notes
The authors declare no competing financial interest.

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