

Hierarchical Ni-Mn Double Layered/Graphene Oxide with Excellent Energy Density for Highly Capacitive Supercapacitors

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Research Article

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ABSTRACT

In this article, a highly capacitive composite electrode material consisting of nickel manganese double layered/graphene oxide (NiMn-LDHs/GO) has been synthesized for supercapacitor energy storage. Various analytical techniques, including X-Ray Diffraction (XRD), Raman spectroscopy, High-Resolution Transmission Electron Microscopy (HRTEM), and Scanning Electron Microscopy (SEM), have been employed to characterize the as-synthesized NiMn-LDHs/GO. The microscopic images obtained using HRTEM analysis clearly reveal the formation of a lattice fringe pattern (lattice spacing of ~0.22 nm) for GO, while SEM images show a highly porous nature.

The super-capacitive performance of the as-synthesized electrode material has been evaluated using an electrochemical workstation comprising of a 3-electrode system. The working electrode, made up of NiMn-LDHs/GO (active material) on Ni foil (working electrode) with the help of PVDF (binder), has shown a specific capacitance of 1964 Fg⁻¹ at a current density of 1 Ag⁻¹ with the Galvanostatic Charging/Discharging (GCD) technique. It has also shown remarkable cyclic stability with a capacitance retention of 96% after 5000-cycles. The high-power density (401 Wkg⁻¹) and energy density (17.78 Whkg⁻¹) signify the excellent electrochemical supercapacitor behaviour in charge storage applications.

Keywords: Super-capacitive performance; Graphene; Nickel manganese double layered/graphene oxide; Physical and chemical characterization; Specific conductance; Energy density; Capacitance stability

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INTRODUCTION

Supercapacitors, also known as ultracapacitors, are energy storage devices that can store and release large amounts of electrical energy in a short amount of time [1]. They are increasingly explored as an alternative to batteries in a variety of applications (including electric vehicles, renewable energy systems, and portable electronics) due to their high flexibility, extraordinary power density, long cycle lifetime with remarkable mechanical properties, fast charge/discharge foldability and conformability, which play a key role in the future electrical energy storage field.

Hierarchical Ni-Mn Double Layered Hydroxide (NMDH) is a type of metal hydroxide that consists of multiple layers of nickel and manganese ions [2]. This material has a high specific capacitance due to the double-layer charge storage mechanism, where the ions accumulate at the surface of the material. The hierarchical structure of NMDH enhances the ion diffusion rate, resulting in faster charge and discharge rates. Additionally, NMDH is stable and has good cycling performance [3].

Graphene oxide is a two-dimensional carbon material with a high surface area and good electrical conductivity [4]. It acts as a conductive matrix that enhances the electron transfer rate and provides a large surface area for charge storage. Combining hierarchical NMDH with graphene oxide forms a composite material that synergistically enhances the energy storage performance of supercapacitors.

Hierarchical Ni-Mn double layered (NiMn-LDH) nanosheets/Graphene Oxide (GO) composites consist of ultrathin NiMn-LDH nanosheets grown on the surface of GO, forming a three-dimensional hierarchical structure that enhances the accessibility of active sites and the electron transport [5]. The hierarchical Ni-Mn double layered/graphene oxide composites have shown excellent energy density, making them ideal for use in energy storage applications such as electric vehicles, renewable energy systems, and portable electronics. They also exhibit superior cycling stability and a long-life cycle, which is crucial for practical applications [6].

Moreover, the fabrication of these composites is relatively simple and cost-effective, making them a promising candidate for large-scale production [7].

Herein, we present a simple facile strategy to conduct-layer hierarchical NiMn-LDH/GO composites nanosheet coated on Ni foil. The as-synthesized NiMn-LDH/GO material has been characterized through XRD, Raman spectroscopy. Further, to access the morphology structure [8], the as-synthesized material has been characterized by Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) techniques.

For the application purpose, we adopt Cyclic Voltammetry (CV) and Galvanometric Charging/Discharging (GCD) techniques. Due to better reliability, we preferred GCD techniques with a three-electrode system.

Overall, the hierarchical NiMn-LDH/GO composites show great potential as high-performance electrode materials for supercapacitors and could pave the way for the development of next-generation energy storage devices with improved energy and power density.

MATERIALS AND METHODS

Graphene oxide powder was purchased from Alfa Aesar. Nickel nitrate hexahydrate $[\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$, $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, NH_4F , NaOH , Na_2CO_3 , N-Dimethyl Formamide (N-DMF), nickel foam, Polyvinylidene Fluoride (PVDF) and carbon black were supplied by Sigma-Aldrich Ltd. All the reagents were used without extra purification. Ultrapure Deionized water ($\text{DI} > 18 \text{ M}\Omega \text{ cm}^{-1}$, Millipore Q system) was used for the preparation of all solutions required during characterizations and experimental procedures.

Synthesis of the NiMn-LDH/graphene oxide hierarchical structure

NiMn-LDH/Graphene was synthesized by two steps. Firstly, 10 mg of Gopowder was dissolved in 250 mL of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (a total concentration of 0.005 M) molar ratio (3:1), and NH_4F (0.020 M) followed by ultrasonication for 80 min at room temperature. Secondly 50 ml of NaOH (0.010 M) and Na_2CO_3 (0.05 M) was added drop wise over 6 h into the above solution with vigorous stirring. Further, it was kept at room temperature for 2 h; the obtained solution was collected in a clean vessel and centrifuged further at 10,000 rpm for 15 min. The centrifuged solution was washed through DI water until the $\text{pH} \sim 7$ and dried at room temperature. The overall process is represented in Figure 1.

Figure 1. Illustration of the strategic pathway for the synthesis of NiMn-LDH/GO.



Fabrication of NiMn-LDH/GO electrode

Take active material (NiMn-LDH/GO) (90 wt%), (PVDF) binder (5 wt%) and carbon black (5 wt%) were dispersed in N-DMF solvent. Next the solution was stirred for 1 h for homogeneous mixture. Further, the prepared solution was coated on Ni foam and dried in room temperature for 3 h, as shown in Figure 2. The total mass loaded on the Ni foam was $\sim 1 \text{ mg}$.

Figure 2. Schematic of NiMn-LDH/GO electrode at the Ni foam.

Electrochemical testing

Electrochemical experiments have been performed on the CHI-660C multichannel workstation with a three-electrode system using Pt wire and Ag/AgCl as a counter and reference electrode respectively. Here Ni-foam is used as working electrode. All the electrochemical measurements were done in 5 M KOH at room temperature. The specific capacitance can be calculated using formula:

$C_m = I \times \Delta t / \Delta V \times m$ (Fg^{-1}) [9,10], where I , m , ΔV and Δt represent the current, mass, voltage window and discharge respectively.

Characterizations techniques

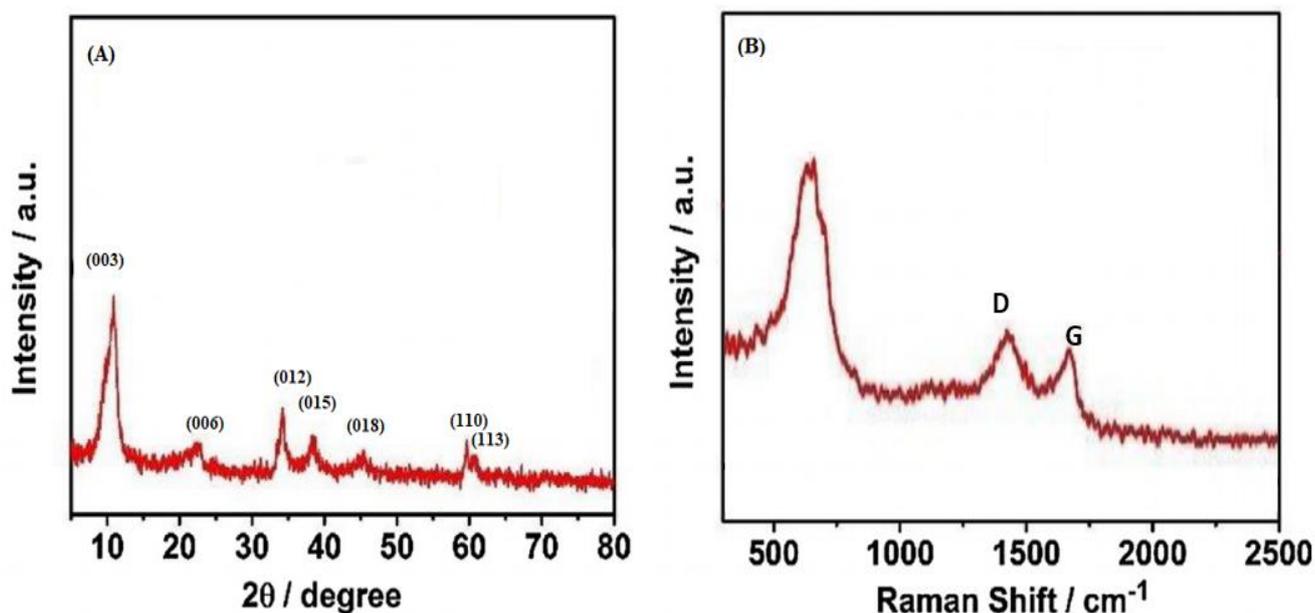
The products were characterized by Scanning Electron Microscopy (SEM, ZEISS) [9], and high-resolution transmission electron microscopy (HRTEM, JEM-2010). X-ray powder diffraction method, through analytical X-ray diffractometer using Cu-K α radiation ($\lambda \sim 1.5406 \text{ \AA}$ at 40-kV and 30-mA), was in 2θ range of 10° - 80° . Raman spectrum was recorded at room temperature with an Nd: YAG laser excitation ($\lambda = 532 \text{ nm}$) using a micro-Raman spectrometer (Renishaw, Raman systems). The N₂ adsorption-desorption isotherms and the pore size distributions were characterized by Brunauer-Emmett-Teller method (micromeritics FlowPrep 060, Gemini VII, USA).

RESULTS AND DISCUSSION

Structural and morphological characterizations

To analyze the phase and crystal structure of the as-prepared electrode material, XRD was performed. As shown in Figure 3A, the obtained electrode material exhibited diffraction peaks at 11.34° , 22.74° , 34.41° , 38.76° , 45.98° , 59.98° , and 61.25° , which corresponded well with (003), (006), (012), (015), (018), (110), and (113) planes of materials, respectively, indicating the formation of the NiMnLDH/GO structure [JCPDS card No. 38-0715] [11]. Raman spectroscopy is widely used to analyze the other structural features of NiMnLDH/GO, especially graphene-derived materials. Raman spectra of the as-synthesized NiMnLDH/GO exhibited two characteristic peaks at the D- and G-bands of graphene, at 1349 cm^{-1} and 1585 cm^{-1} , respectively [12], as shown in Figure 3B. The D-band indicates a disordered band, while the G-band reveals the crystallinity of the graphitized network [13]. The presence of metal-oxygen-metal bonds at 674 cm^{-1} suggests the successful deposition of LDH [14]. Notably, the value of R ($R=ID/IG$) is 0.85, confirming that the carbon isotopes are graphitic in nature [15]. The higher value of ID compared to IG indicates the crystalline nature of the electrode material [16].

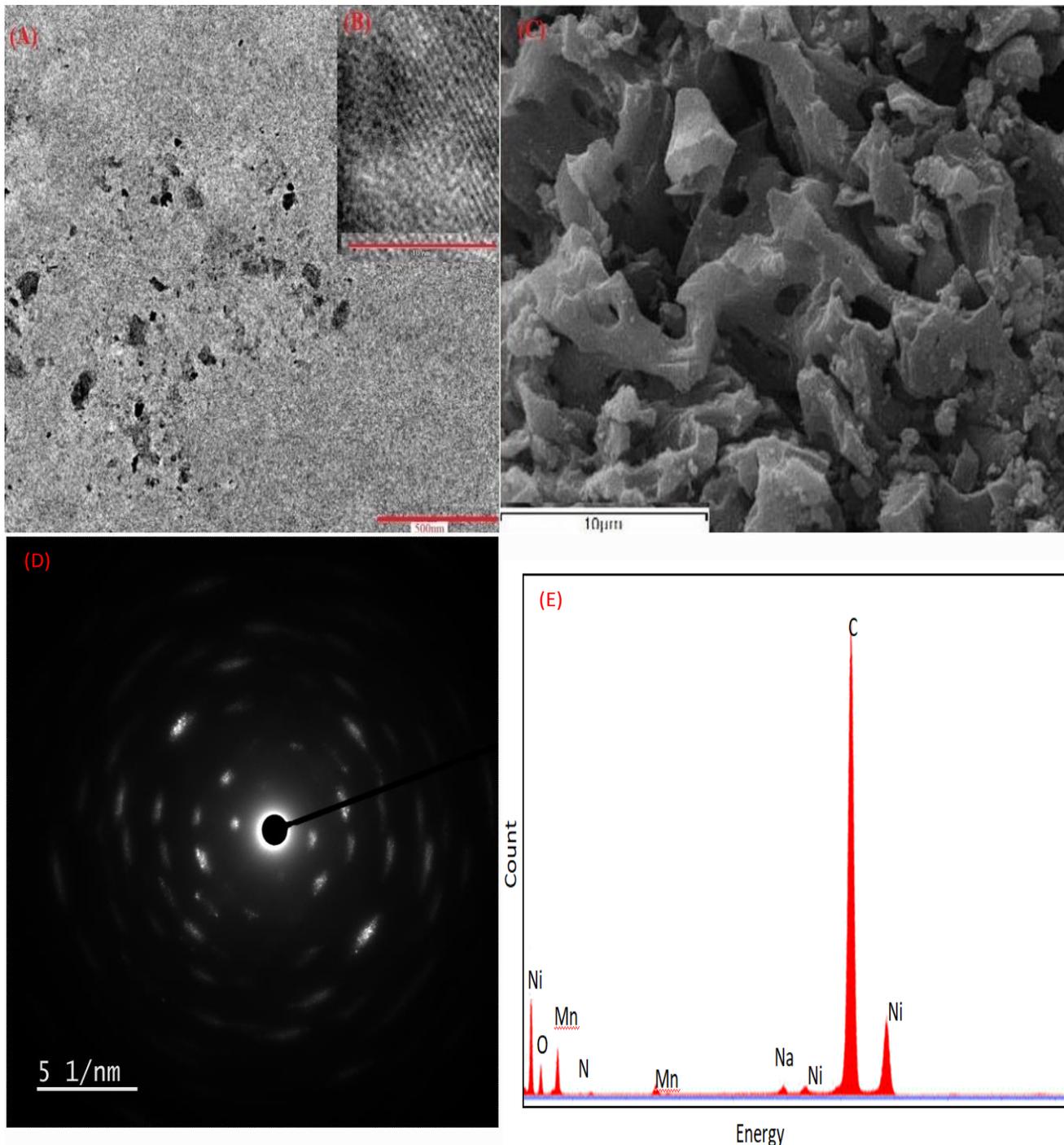
Figure 3. (A) XRD pattern and (B) Raman spectrum of NiMn-LDH/GO.



The particle size, surface morphologies, and structures of the as-prepared NiMn-LDHs/GO were analyzed using TEM, HR-TEM, and SEM images, respectively. TEM and HR-TEM images of NiMn-LDH/GO are shown in Figures 4A and 4B, respectively, where the dark region shows Ni-Mn random crystal on the surface of GO. Surface morphologies and structures are shown in Figure 4C. The flaky nanoparticle nature of LDH is clearly visible, along with an interplanar lattice spacing of about 0.22 nm. The wrinkled region shows layered assembly of LDH and GO. The dark region represents folded nanosheets due to the similarity of their layered stacking geometry, which contributes to the strong anchoring of LDH on GO support. Moreover, the surface morphology suggests the presence of large, irregular, and disordered pores in the as-synthesized NiMn-LDH/GO. The large pore size structure on the surface of the prepared sample is dominant for the charge storage applications like supercapacitors [17]. Figure 4D shows the SEAD pattern of the NiMn-LDHs/GO composite, whereas Figure

4E shows the EDS analysis, which reveals that C has the largest elemental presentation at 41.02%, followed by Ni at 35.32% and Mn at 22.03%.

Figure 4. TEM image (A) bar scale 500 nm and (B) HRTEM image of NiMn-LDH/GO at bar scale 20 nm (C) SEM image at 10 μm scale (D) SEAD pattern of NiMn-LDHs/GO (E) EDS analysis of NiMn-LDHs/GO composite.

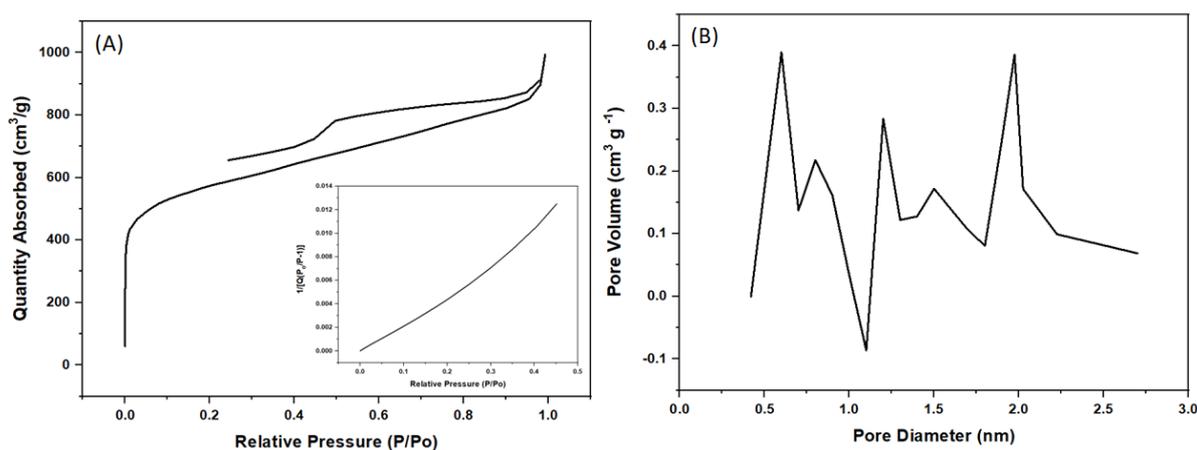


BET analysis

The porosity in the NiMn-LDH/GO composite has been produced with $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ during the synthesis. The surface area and pore structure play a very important role in the supercapacitor applications. The as-

synthesized NiMn-LDH/GO has been examined by N_2 adsorption–desorption using the BET principle. Figure 5A shows the nitrogen adsorption–desorption isotherm of NiMn-LDH/GO, which exhibits a type II- and IV-curve [18]. A type IV isotherm curve occurs when N_2 gases condense in the tiny capillary pores of the prepared sample at pressures below the saturation pressure of the gas, confirming the presence of mesoporous nature [19]. On the other hand, type II represents microporous structure [20]. The microporous and mesoporous behaviour is favourable for supercapacitor applications [21]. Figure 5A (inset) illustrates a straight line for the quantity absorbed vs. relative pressure (P/P_0), which is in good agreement for determining the total surface area [22]. To explore pore diameter vs pore volume, Figure 5B depicts the average pore size diameter and volume of 1.3-nm and $0.15 \text{ cm}^3\text{g}^{-1}$, respectively. The BET isotherm curve reveals that the surface area possesses a value of $\sim 2940 \text{ m}^2\text{g}^{-1}$, which is in good agreement for supercapacitor applications (Figures 6A-6D).

Figure 5. (A) N_2 adsorption–desorption analysis isotherm (inset showing a relation between relative pressure (P/P_0) versus $1/[Q(P_0/P-1)]$), (B) BJH plot; pore size distribution plot NiMn-LDH/Go composite.



Electrochemical analysis

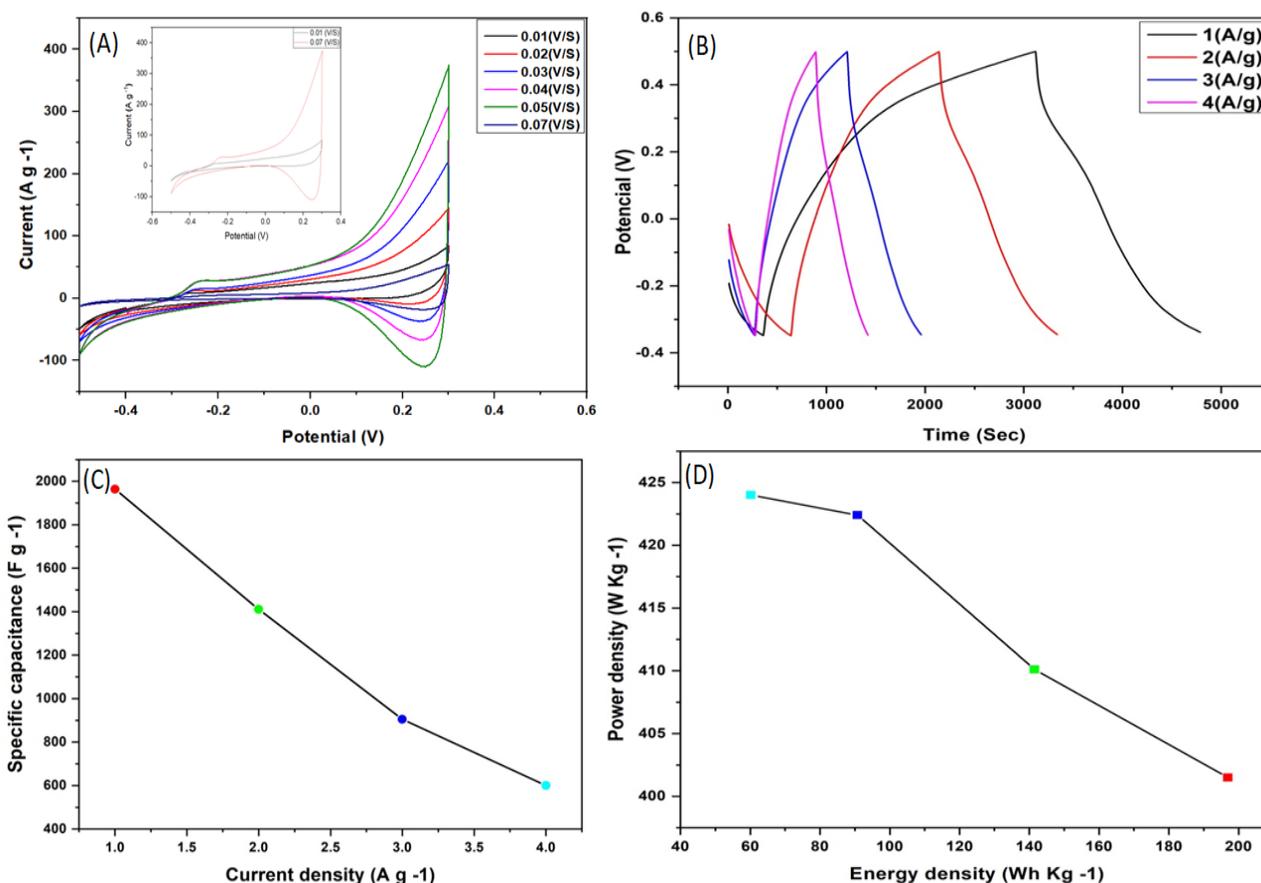
The charge-storage mechanism of the NiMn-LDH/Graphene electrode material in a supercapacitor involves both pseudo-capacitance and double-layer capacitance contributions [23].

In the pseudo-capacitance contribution, the electrode material undergoes reversible redox reactions at the electrode/electrolyte interface, leading to the transfer of charge between the electrode material and electrolyte [24]. Specifically, in the NiMn-LDH/Graphene composite electrode material, the nickel and manganese ions in the Double-Layered Hydroxides (LDHs) can undergo reversible redox reactions, resulting in the storage of charge.

In the double-layer capacitance contribution, charge is stored in the electric double layer formed at the electrode/electrolyte interface due to the adsorption/desorption of electrolyte ions onto/from the surface of the electrode material [25]. The Graphene Oxide (GO) component of the NiMn-LDH/Graphene composite electrode material provides a high surface area and excellent conductivity, which facilitates the formation of the electric double layer and enhances the double-layer capacitance contribution [26].

The electrochemical responses of the NiMn-LDH/GO composite have been characterized by CV and Galvanostatic Charge-Discharge (GCD) measurements at the same potential window (-0.5 to $+0.6$ V). The CV characterization of the NiMn-LDH/GO composite was operated at various scan rates (i.e., 0.01, 0.02, 0.03, 0.04, 0.05, and 0.07 V/s), as shown in Figure 6A.

Figure 6. A) Cyclic Voltammeter (CV) characterization of NiMn-LDH/GO composite at different scan rate range from (0.01-0.07 V/s). B) Charge/discharge curve of NiMn-LDH/GO composite at three different current densities ranging from (1A/g to 4A/g). C) Specific capacitance (F/g) vs. Charge/discharge of NiMn-LDH/GO composite. D) Ragone plot for NiMn-LDH/GO composite. **Note:** — 0.01 (V/S), — 0.02 (V/S), — 0.03 (V/S), — 0.04 (V/S), — 0.05 (V/S), — 0.07 (V/S), — 1 (A/g), — 2 (A/g), — 3 (A/g), — 4 (A/g).



The CV experiment provides relevant information regarding the charging/discharging behaviour of the as-synthesized NiMn-LDH/GO. Due to the presence of metallic properties, the CV curves exhibit redox peaks, confirming the behaviour of pseudo-type capacitance. Figure 6A (inset) shows the first and last cycle at scan rates of 0.01 and 0.07 V/s. Notably, at a very large scan rate, no distortion appears because of the large pore size. This event exhibits perfect supercapacitor behaviour of pseudo-capacitors.

To examine the specific capacitance, we performed the Galvanostatic Charge-Discharge (GCD) technique shown in Figure 6B. It is clearly seen that the NiMn-LDH/GO composite illustrates the longest charge/discharge time, implying the highest specific capacitance at different current densities of 1, 2, 3, and 4 Ag⁻¹. It shows that the discharge times decrease with the increase of the current density from 1 to 4 Ag⁻¹, which can be attributed to the limited diffusion rate of the ions. From the slope of the discharge curve, Figure 6C exhibits the specific capacitance curves of the NiMn-LDH/GO composite that provide excellent specific capacity of 1964 Fg⁻¹ at 1 Ag⁻¹ current density, shown in Table 1. Further, the supercapacitor devices comprised of NiMn-LDH/GO show 4% degradation in performance after 5000 cycles at a current density of 1 Ag⁻¹

(Figure 7). Figure 6C represents the Ragone plot against charging/discharging techniques, showing a remarkable energy density of 196.94 Whkg⁻¹ at 424.5 Wkg⁻¹ power density calculated from

$$E = C_s \times \Delta V^2 / 7.2 \text{ (Wh kg}^{-1}\text{) and}$$

$$P = E \times 3600 / \Delta t \text{ (W kg}^{-1}\text{) respectively.}$$

Specific capacitance, energy, and power density results are shown in Table 1. These results depict that the NiMn-LDH/GO composite is a high-performance, promising electrode material for electrochemical supercapacitor applications. Table 2 provides different metal-based supercapacitors with their specific capacitance.

Figure 7. Cycling stability of NiMn-LDH/GO electrode at current density 1.0 Ag⁻¹.

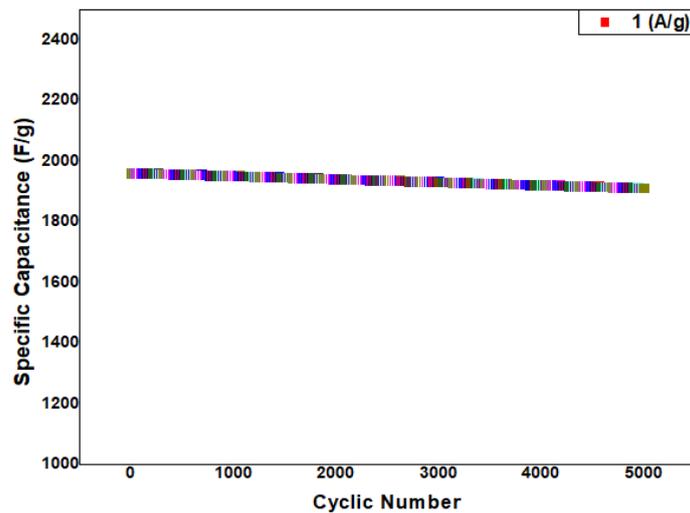


Table 1. Summarized values of other parameters calculated by GCD technique.

Current density (Ag ⁻¹)	Specific capacitance (Cm) (Fg ⁻¹)	Energy density (E) (Whkg ⁻¹)	Power density (P) (Wkg ⁻¹)
1	1964	196.94	424.5
2	1411	141.49	422.1
3	905	90.75	441.4
4	600	60.16	401

Table 2. Comparison table of different metal-based supercapacitor electrode.

Composite material	Specific capacitance (F g ⁻¹)	Current density (A g ⁻¹)	Electrolyte	References
MnMoO ₄ /CoMoO ₄	187	1	2 M NaOH	[27]
MnCo ₂ O ₄ .5NiCo ₂ O ₄	325	1	3 M KOH	[28]
CoWO ₄ -Ni ₃	271	1	6 M KOH	[29]
ZnNnCO ₄ /CWO ₄	309	1	2 M KOH	[30]
Core-shell CuCo ₂ O ₄ /MnO ₂ nanowires	327	1.25	3 M KOH	[31]
Starfish-shaped Co ₃ O ₄ /ZnFe ₂ O ₄	326	1	6 M KOH	[32]
Co-Al LDH/graphene	712	1	6 M KOH	[33]

Co-Al LDH/Pt	734	3	2 M KOH	[34]
Co-Al LDH/graphene	772	1	6 M KOH	[35]
CoAl-LDH/PEDOT	672	1	6 M KOH	[36]
NiAl LDH	795	0.5	1 M KOH	[37]
CoAl LDH/graphene	479	1	6 M KOH	[38]
Hollow sphere NiMn-LDH-12	951	1	3 M KOH	[39]
Hollow shelled Mn-Cu-Al-oxide	319	1	1 M NaOH	[40]
NiMn-LDHs/GO	1964	1	5 M KOH	Present work

CONCLUSION

In summary, the present study illustrates a simple, facile, and cost-effective procedure for synthesizing a supercapacitor electrode material NiMn-LDH/GO. This technology is useful for large power devices. The as-synthesized electrode material achieves remarkable electrocapacitive performance with a large specific capacitance of 196 Fg^{-1} at a current density of 1.0 Ag^{-1} . Moreover, the as-synthesized NiMn-LDH/GO has shown excellent capacitive retention after 5000 cycles, which clearly marks its sustainable electrocapacitive nature. However, it may exhibit low specific capacitance after 5000-cycles and change our charging and discharging behaviour after a large current density. The obtained capacitive electrode material delivers an ultrahigh energy density of 196.94 Whkg^{-1} with a reasonably excellent power density of 401 Wkg^{-1} and hence offers outstanding potential for practical applications in energy storage devices such as supercapacitors. This study is useful for devices that require maximum power and energy, with a notable specific capacitance. It is also useful for studying the "Ni" series for energy storage applications.

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DISCLAIMER

The views expressed in this article reflect those of the authors and do not reflect the official views of the institutions where they work or previously worked.

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