Hierarchical NiMn Double Layered/Graphene with Excellent Energy Density for Highly Capacitive Supercapacitors

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Abstract

In the present article, highly capacitive NiMn-LDHs/GO composite of electrode material has been synthesized for supercapacitor energy storage. Various analytical techniques (particularly X-ray diffraction (XRD), Raman spectroscopy, high resolution transmission electron microscopy (HRTEM), and scanning electron microscope (SEM)) have been employed to characterize the as-synthesized NiMn-LDHs/GO. The Microscopic images obtained using HRTEM analysis clearly reveal the formation of lattice fringe pattern (lattice spacing as ~ 0.22 nm) for GO, whereas SEM images shows highly porous nature. The super-capacitive performance of the as-synthesized electrode material have been accessed through an electrochemical work station 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 specific capacitance of 1964 F g^{-1} at current density of 1 A g^{-1} with Galvanostatic charging/discharging (GCD) technique. It has also shown remarkable cyclic stability with a capacitance retention of 98% after 2000 cycles. The high-power density (401 W/kg) and energy density (17.78 Wh/kg) signify the high-level electrochemical supercapacitor behaviour in charge storage applications.

1. Introduction

In the last decennium, portable electronic devices such as supercapacitors (SCs), solar cells, and lithium-ion batteries have gained much attention because of their energy storage, high flexibility, extraordinary power density, long cycle lifetime with remarkable mechanical properties, fast charge/discharge foldability, and conformability. These play a key role in the future electrical energy storage field (Pushparaj, Shaijumon, Kumar, Murugesan, Ci, Vajtai, Linhardt, Nalamasu and Ajayan, 2007, Miller, 2012, El-Kady, Strong, Dubin and Kaner, 2012). Among these devices, SCs have been dynamically trusted due to the electrical properties and mechanical honesty of the constitutive materials and their original assembly into a detached and binderless framework (Chen, Rakhi, Hu, Xie, Cui and Alshareef, 2011, Bae, Song, Park, Kim, Liu and Wang, 2011, Choi, Hong, Hong, Hammond and Park, 2011). Dignity of high energy density, high specific capacitance electric double layer capacitors (EDLCs), and pseudo capacitors attached much awareness. Owing to large surface area and more reaction sites, 2D materials, such as layered double hydroxides (LDHs) (Chen, Zhao, Wei, Li and Mi, 2020, Yin, Li, Zhang, Zhao, Luo, Shao and Han, 2020, Xu, Kong, Zhou, Zheng, Huo and Strømme, 2018, Yang, Ye, Liang, Wu, Long, Xu and Wang, 2020), transition metal oxides (TMOs) (Li, Han, Yi, He and Li, 2019, Zhang, Zhang, Sun, Sun and Liu, 2018, Bandgar, Vadiyar, Ling, Chang, Han, Ghule and Kolekar, 2018, Chen, Wang, Luo, Gao, Huang, Zeng and Zhu, 2019), and transition metal sulphide (TMSs) (Bulakhe, Arote, Kwon, Park and In, 2020, Zheng, Tian, Sarwar, Luo and Zhang, 2020, Rafai, Qiao, Naveed, Wang, Younas, Khalid and Cao, 2019, Yasoda, Kumar, Kumar, Ghosh and Batabyal, 2021) have been recommended in the field of energy storages devices. To achieve high specific capacity and rate capability, most of research performed LDHs type charismatic electrode material for SCs applications by reason of their low cost, non-toxicity, tuneable chemical composition, and environmental friendly nature (Zhang, Chen, Hui, San Hui and Lee, 2017, Li,

San Hui, Hui, Xia, Fu and Cho, 2017). Zhi et al. 2018) proposed holey NiCo-LDHs thin sheets with $6.37\text{F}/\text{cm}^2$, $25\text{F}/\text{g}$ and $249\text{F}/\text{cm}^2$ areal, gravimetric and volumetric specific capacitance respectively.

Herein, a simple facile strategy is presented to conduct-layer NiMn-LDH/Graphene oxide nanosheet arrays grown on Ni foam. The as-synthesized NiMn-LDH/GO material has been characterized through XRD, Raman spectroscopy. To access the morphology structure, the as-synthesized material has been characterized by scanning electron microscopy (SEM) and TEM techniques (Shandilya and Kumar, 2010). The application purpose adopted cyclic Voltammetry (CV) and galvanometric charging/discharging (GCD) techniques. GCD techniques are preferred with a three-electrode system due to better reliability.

2. Experimental Section

2.1 Materials:

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.

2.2 Synthesis of the NiMn-LDH/Graphene Hierarchical Structure:

NiMn-LDH/Graphene was synthesized by simple two steps. Firstly, 10 mg of Go powder 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), 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 hours into the above solution with vigorous stirring. Further, it was kept to be cooled naturally to room temperature for 24 hours, the obtained solution was collected in a clean vessel and centrifuged further at 10,000 rpm for 15 minutes. The centrifuged solution was washed and dried at room temperature.

2.3 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. Thereafter the solution was stirred for 1 hour for homogeneous mixture. Further, the prepared solution was coated on Ni foam and dried at room temperature for 3 hours. The total mass loaded on the Ni foam was $\sim 1\text{mg}$.

2.4 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 used as working electrode. All the electrochemical measurements were done in 5 M KOH at room

temperature. The specific capacitance can be calculated as $C_m = \frac{I \times \Delta t}{\Delta V \times m}$ (F/g). Here, I, m, ΔV , and Δt represent the current, mass, voltage window, and discharge, respectively.

3 Characterizations Techniques:

The products were characterized by scanning electron microscopy (SEM, ZEISS), and high-resolution transmission electron microscopy (HRTEM, JEM-2010). X-ray powder diffraction method, through panalytical x-ray diffractometer using Cu-K α radiation ($\lambda \sim 1.5406 \text{ \AA}$ at 40 kV and 30 mA), in 2θ range of 10° to 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).

3. Results And Discussion

3.1 Structural and morphological characterizations:

To elucidate the analysis of phase and crystal structure of the as-prepared electrode material was evaluated by XRD. As shown in Fig. 1a, it is obviously seen that the XRD pattern of the obtained electrode material shows the diffraction peaks at 11.34° , 22.74° , 34.41° , 38.76° , 45.98° , 59.98° and 61.25° are accorded well with (003), (006), (012), (015), (018), (110) and (113) planes of materials, respectively, which can represent the formation of NiMnLDH/GO structure [JCPDS card No. 38-0715] (Zhao, Chen, Xu, Shao, Zhang, Wei, Ma, Wei, Evans and Duan, 2014). The other structural features of NiMnLDH/GO especially graphene-derived materials have been widely used by Raman spectroscopy. Raman spectra of the as-synthesized NiMnLDH/GO have been demonstrated two characteristic peaks at D and G band of graphene at 1349 cm^{-1} and 1585 cm^{-1} respectively shown in Fig.1(b). The D band appears due to disordered band whereas g band reveals crystallinity of the graphitized network. The presence of metal-oxygen-metal bonds at 674 cm^{-1} occurs for binary hybrids [37], indicating the successful deposition of

LDH. It is noteworthy that the value of R , ($R = \frac{I_D}{I_G}$) is 0.85, which confirms that the carbon isotopes are shown to be more graphitic in nature.

The particle size, surface morphologies, and structures of the as-prepared NiMn-LDHs/GO were also performed using TEM, HR-TEM, and SEM images, respectively. Figs. 2(A) and 2(B) show TEM and HR-TEM images of NiMn-LDH/GO, respectively, whereas surface morphologies and structures are shown in Fig. 2(C). The flaky nanoparticle nature of LDH is clearly visible along with interplanar lattice spacing at 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 strong anchoring of LDH on GO support. Moreover, 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 has been dominant for the charge storage applications like supercapacitors.

3.2 Electrochemical Analysis:

The electrochemical responses of NiMn-LDH/GO composite have been characterized by CV and galvanostatic charge/discharge measurement. The CV characterization of NiMn-LDH/GO composite has operated between -0.5 to +0.35 under various scan rate (i.e. 0.01, 0.02, 0.03, 0.04, 0.05 and 0.07 V/s) as shown in Fig.3 (A) The CV experiment embellishes the relevant information regarding the charging/discharging behaviour of the as-synthesized NiMn-LDH/GO. Due to presence of metallic properties CV curves exhibits redox peak. It confirms the behaviour of Pseudo type capacitance. Notably, at a very large scan rate no distortions appear because of large pore size. This event exhibits perfect supercapacitor behaviour of Pseudo-capacitors. To examine the specific capacitance, the researchers performed the galvanostatic charge-discharge (GCD) technique, as shown in Fig. 3 (B and C). From the slop of discharge curve, Fig. 3 (B and C) exhibit the charging/discharging curves of NiMn-LDH/GO composite have shown excellent specific capacity 1964 F/g, 1411 F/g, 905 F/g and 600 F/g at 1 A/g, 2 A/g, 3 A/g and 4 A/g current density, respectively. Further, the supercapacitor devices comprised of NiMn-LDH/GO showed 2% degradation in performance after 2000 cycles at current density at 1A/g (Figure 4). Fig.3(c) represents the Ragone plot against charging/discharging techniques. This showed remarkable energy density of 196.94 (Wh/kg) at 424.5 (W/kg) power density calculated from $E = C_s \times \Delta V^2 / 7.2$ (Wh/kg) and $P = E \times 3600 / \Delta t$ (W/kg), respectively. Specific capacitance, energy, and power density results are shown in Table 1. These results depict that NiMn-LDH/GO composite are high performance, promising electrode materials for electrochemical supercapacitors applications.

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

Current density (A/g)	Specific capacitance (C _m) (F/g)	Energy density (E) (Wh/kg)	Power density (P) (W/kg)
1	1964	196.94	424.5
2	1411	141.49	422.1
3	905	90.75	441.4
4	600	60.16	401.0

4. Conclusion

In summary, the present study illustrates a simple, facile, and cost-effective procedure for synthesis of a supercapacitor electrode material NiMn-LDH/GO. This technology is useful in large power devices. The as-synthesized electrode material achieves remarkable electrocapacitive performance with large specific capacitance of 1964 F/g at a current density of 1.0 A/g. Moreover, the as-synthesized NiMn-LDH/GO have shown excellent capacitive retention after 2000 cycles, which clearly embarks its sustainable electrocapacitive nature. It can behave low specific capacitance after 2000 cycles and change our charging and discharging behavior after large current density. The obtained capacitive electrode material

delivers an ultrahigh energy density of 196.94 Wh/kg with a reasonably excellent power density of 401 W/kg and, henceforth, offers an outstanding potential for the practical applications in energy storage devices like supercapacitors.

This study is useful for maximum power as well as energy-required devices with notable specific capacitance. It is also useful for study 'Ni' series for energy storage applications.

Declarations

Availability of data and material

All the data and materials used is presented in this manuscript.

Competing interests

Authors declare no competing interests.

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Authors' contributions

Gopal Krishna Gupta and Arpita Dwivedi carried out the experimental work. Dr. Kaushik Kumar Shandilya acting as the corresponding author and provided guidance and conceptualization. Dr. Kaushik Kumar Shandilya and Dr. Anu Sharma contributed to writing the manuscript.

Authors' information

This information is provided on the first page of this manuscript.

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References

1. Pushparaj, V. L., Shaijumon, M. M., Kumar, A., Murugesan, S., Ci, L., Vajtai, R., Linhardt, R. J., Nalamasu, O., and Ajayan, P. M. (2007). "Flexible energy storage devices based on nanocomposite

- paper." *Proceedings of the National Academy of Sciences*, 104(34), 13574-13577.
2. Miller, J. R. (2012). "Valuing reversible energy storage." *Science*, 335(6074), 1312-1313.
 3. El-Kady, M. F., Strong, V., Dubin, S., and Kaner, R. B. (2012). "Laser scribing of high-performance and flexible graphene-based electrochemical capacitors." *Science*, 335(6074), 1326-1330.
 4. Chen, W., Rakhi, R., Hu, L., Xie, X., Cui, Y., and Alshareef, H. N. (2011). "High-performance nanostructured supercapacitors on a sponge." *Nano Lett.*, 11(12), 5165-5172.
 5. Bae, J., Song, M. K., Park, Y. J., Kim, J. M., Liu, M., and Wang, Z. L. (2011). "Fiber supercapacitors made of nanowire-fiber hybrid structures for wearable/flexible energy storage." *Angew. Chem. Int. Ed.*, 50(7), 1683-1687.
 6. Choi, B. G., Hong, J., Hong, W. H., Hammond, P. T., and Park, H. (2011). "Facilitated ion transport in all-solid-state flexible supercapacitors." *ACS nano*, 5(9), 7205-7213.
 7. Chen, S., Zhao, L., Wei, W., Li, Y., and Mi, L. (2020). "A novel strategy to synthesize NiCo layered double hydroxide nanotube from metal organic framework composite for high-performance supercapacitor." *Journal of Alloys and Compounds*, 831, 154794.
 8. Yin, Q., Li, D., Zhang, J., Zhao, Y., Luo, J., Shao, M., and Han, J. (2020). "An all-solid-state fiber-type supercapacitor based on hierarchical Ni/NiO@ CoNi-layered double hydroxide core-shell nanoarrays." *Journal of Alloys and Compounds*, 813, 152187.
 9. Xu, C., Kong, X., Zhou, S., Zheng, B., Huo, F., and Strømme, M. (2018). "Interweaving metal-organic framework-templated Co-Ni layered double hydroxide nanocages with nanocellulose and carbon nanotubes to make flexible and foldable electrodes for energy storage devices." *Journal of Materials Chemistry A*, 6(47), 24050-24057.
 10. Yang, T., Ye, Q., Liang, Y., Wu, L., Long, X., Xu, X., and Wang, F. (2020). "Graded holey Nickel Cobalt layered double hydroxide nanosheet array electrode with high mass loading for high-energy-density all-solid-state supercapacitors." *Journal of Power Sources*, 449, 227590.
 11. Li, Y., Han, X., Yi, T., He, Y., and Li, X. (2019). "Review and prospect of NiCo₂O₄-based composite materials for supercapacitor electrodes." *Journal of energy chemistry*, 31, 54-78.
 12. Zhang, X., Zhang, Z., Sun, S., Sun, Q., and Liu, X. (2018). "Hierarchical 3D NiFe₂O₄@ MnO₂ core-shell nanosheet arrays on Ni foam for high-performance asymmetric supercapacitors." *Dalton transactions*, 47(7), 2266-2273.
 13. Bandgar, S. B., Vadiyar, M. M., Ling, Y.-C., Chang, J.-Y., Han, S.-H., Ghule, A. V., and Kolekar, S. S. (2018). "Metal precursor dependent synthesis of NiFe₂O₄ thin films for high-performance flexible symmetric supercapacitor." *ACS Applied Energy Materials*, 1(2), 638-648.
 14. Chen, C., Wang, S., Luo, X., Gao, W., Huang, G., Zeng, Y., and Zhu, Z. (2019). "Reduced ZnCo₂O₄@ NiMoO₄·H₂O heterostructure electrodes with modulating oxygen vacancies for enhanced aqueous asymmetric supercapacitors." *Journal of Power Sources*, 409, 112-122.
 15. Bulakhe, R. N., Arote, S. A., Kwon, B., Park, S., and In, I. (2020). "Facile synthesis of nickel cobalt sulfide nano flowers for high performance supercapacitor applications." *Materials Today Chemistry*, 15, 100210.

16. Zheng, Y., Tian, Y., Sarwar, S., Luo, J., and Zhang, X. (2020). "Carbon nanotubes decorated NiSe₂ nanosheets for high-performance supercapacitors." *Journal of Power Sources*, 452, 227793.
17. Rafai, S., Qiao, C., Naveed, M., Wang, Z., Younas, W., Khalid, S., and Cao, C. (2019). "Microwave-anion-exchange route to ultrathin cobalt-nickel-sulfide nanosheets for hybrid supercapacitors." *Chem. Eng. J.*, 362, 576-587.
18. Yasoda, K., Kumar, S., Kumar, M., Ghosh, K., and Batabyal, S. (2021). "Fabrication of MnS/GO/PANI nanocomposites on a highly conducting graphite electrode for supercapacitor application." *Materials Today Chemistry*, 19, 100394.
19. Zhang, L., Chen, R., Hui, K. N., San Hui, K., and Lee, H. (2017). "Hierarchical ultrathin NiAl layered double hydroxide nanosheet arrays on carbon nanotube paper as advanced hybrid electrode for high performance hybrid capacitors." *Chem. Eng. J.*, 325, 554-563.
20. Li, L., San Hui, K., Hui, K. N., Xia, Q., Fu, J., and Cho, Y.-R. (2017). "Facile synthesis of NiAl layered double hydroxide nanoplates for high-performance asymmetric supercapacitor." *Journal of Alloys and Compounds*, 721, 803-812.
21. Zhi, L., Zhang, W., Dang, L., Sun, J., Shi, F., Xu, H., Liu, Z., and Lei, Z. (2018). "Holey nickel-cobalt layered double hydroxide thin sheets with ultrahigh areal capacitance." *Journal of Power Sources*, 387, 108-116.
22. Zhao, J., Chen, J., Xu, S., Shao, M., Zhang, Q., Wei, F., Ma, J., Wei, M., Evans, D. G., and Duan, X. (2014). "Hierarchical NiMn layered double hydroxide/carbon nanotubes architecture with superb energy density for flexible supercapacitors." *Adv. Funct. Mater.*, 24(20), 2938-2946.
23. Shandilya, K., Kumar, A. (2010). "Morphology of single inhalable particle inside public transit biodiesel fueled bus." *Journal of Environmental Sciences*, 22 (2), 263-270.

Figures

Figure 1

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

Figure 2

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 micro metre scale.

Figure 3

(a) Cyclic voltammeter 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.

Figure 4

Cycling stability of NiMn-LDH/GO electrode at current density 1.0 A/g.