FABRICATION OF NANOSHEET SHAPED NiCo2O4@MnO2 ELECTRODE PERFORMANCE FOR ASYMMETRIC SUPERCAPACITOR ENERGY STORAGE APPLICATIONS

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Abstract

Using a microwave synthesis, we prepared a stable NiCo₂O₄@MnO₂ nanosheet heterostructure with good electrical conductivity. The NiCo₂O₄@MnO₂ heterostructure exhibits distinctive features such as a stable nanostructure, rapid electron transport, and a multitude of ion diffusion pathways. The electrode demonstrates a notable specific capacitance of 1215 F g⁻¹, along with a cycling stability of 98% following 10000 cycles. The incorporation of MnO₂ is attributed to the material's significant surface area, appropriate pore structure, and notably strong electron conductivity. The fabrication of a symmetric supercapacitor with exceptional electrochemical properties involves the utilization of a heterostructure composed of NiCo₂O₄@MnO₂ as the positive electrode, activated carbon as the negative electrode, and electrolyte consisting of PVA/KOH gel. The supercapacitor exhibits an increased operational range of 1.7 V, a maximum energy density of 49.3 Wh kg⁻¹, a maximum power density of 20.3 kW kg⁻¹, and a favourable capacitance retention of 90% following 10,000 cycles.

1. INTRODUCTION

Electrochemical energy storage systems with high power and energy density are becoming increasingly relevant as the modern industry continues to expand at a rapid pace[1,2] Supercapacitors are expected to meet these demands more reliably than conventional energy storage devices due to their rapid charge-discharge, extended cycle life, high power density, and low environmental impact[3-7].

According to the method used to store the charge, supercapacitors can be roughly classified into two categories: electric double-layer capacitors (EDLCs) and pseudocapacitors. Energy-dense carbon-based materials (EDLCs) like carbon nanotubes and active carbon absorb electrostatic charge at the electrolyte-electrode interface to store electrical energy [8,9].

Fast and reversible faradaic redox processes at the surface of electrode materials are exploited by pseudocapacitors such as transition metal oxides, hydroxides, sulfides, and polymers [10-14].

Due to its large theoretical capacity and remarkable electrochemical activity, the ternary transition metal oxide NiCo₂O₄ nanoparticles have been intensively researched for use in supercapacitors[15-18]. Furthermore, NiCo₂O₄ materials frequently display a wide variety of forms and orientations[19–20].

Despite this, the enormous quantity of charge storage in NiCo₂O₄ nanomaterials frequently causes the crystal structure to expand or contract greatly during the charge–discharge process [21] Due to its high theoretical specific capacitance (1370 F g-1), abundant supply, and low environmental impact, MnO₂ is another promising material[22-24]. However, its actual application in supercapacitors is limited by MnO₂'s

relatively weak electrical conductivity range of 10⁵ to 10⁶ S cm-1. The energy density decreases when the active sites are underutilized [25].

Two crucial characteristics of supercapacitors are their charging capacity and their cyclic stability. Consequently, the design of the electrode materials has received a lot of focus in order to achieve high capacitance, high energy density, and extended cycle life. A hybrid material is an efficient choice that can capitalize on the benefits that are offered by a variety of materials.

To maximize both working potential and capacitance storage, asymmetric supercapacitors rationally integrate the benefits of battery-type capacitors with electrochemical double-layered capacitors [26]. In this work, we report the preparation of MnO_2 @ NiCo₂O₄ nanosheets by a straightforward microwave method. The goods used in their unprocessed form are put to use as electrode material in supercapacitors. At a current density of 1-10 Ag⁻¹, it demonstrates that the MnO_2 @ NiCo₂O₄ electrode provides a high specific capacitance of 1215 Fg⁻¹.

The as-assembled asymmetric supercapacitor has a capacitance retention of 95% after 10,000 cycles at 5 Ag⁻¹ and an energy density of 49 Wh kg-1. It also has an exceptional power density of 20.43 kW kg-1. An overall method for the development of electrode materials for use in highly efficient asymmetric supercapacitors is presented here.

2. EXPERIMENTAL PROCEDURE

2.1 Synthesis of NiCo₂O₄

The microwave reaction and thermal annealing approach was used to produce the NiCo₂O₄ electrodes with needle-like arrays. First 1 mmol of Co(NO₃)₂. $.6H_2O$, and 0.5 mmol of Ni(NO₃)₂. $.6H_2O$, taken in a clean beaker and this precursor is dissolved in a distilled water and ethanol stir for 30 minutes .

Now add 4.5 mmol of NaOH to the above prepared homogenous solution and again magnetic stirring was taking place for 30-40 minutes. The resultant solution was kept in the LG microwave oven (MH-4048 GW) to undergo microwave irradiation.

The output power was maintained at 800 W with an operating frequency of 2.45 GHz. The irradiation was continued for 5 min step by step process and then it was left to cool down to the ambient temperature. To remove the ions and byproducts, the obtained product was subjected to washing with double distilled water and ethanol. In order to dry, the product was kept in a hot-air oven at 60°C for 12 h.

The dried product was grinded well and kept in a muffle furnace for annealing at 400°C for 4 h. After annealing, dark green colour powder was obtained.

2.2 Preparation of the NiCo₂O₄@MnO₂

Manganese Acetate (1 mmol) and NiCo₂O₄ was first dissolved in DMF(di-methyl formamide) stir for 30 minutes to create the reaction solution, Then the remaining synthesis procedure such as microwave process, drying, and annealing were followed as similar to the procedure which was followed for the NiCo₂O₄ synthesis.

2.3 Materials Characterization

Using a scanning electron microscope (FESEM, Hitachi-S4800) with an acceleration voltage of 5 kV, the morphology of the material was studied. Transmission electron microscopy (TEM, Hitachi-HT7700) at 100 kV and high-resolution transmission electron microscopy (HRTEM, FEI Tacnai G2) at 200 kV were used to establish the structure of the material. Powder X-ray diffraction (XRD) patterns were collected using a Bruker D8 diffractometer and a CuK radiation source (=1.54060) to determine the crystal structure.

2.4 Electrochemical measurements:

The CHI 660E electrochemical workstation was used to conduct the research in 3 M aqueous KOH solution for the electrochemistry. The reaction was carried out in a three-electrode cell configuration, with a platinum wire counter electrode, a saturated calomel electrode as the reference electrode, and a working electrode fabricated by combining active material (weight 80% sample), conductive material (weight 10% acetylene black), and binder (weight 10% polytetrafluoroethylene). Active material mass loading was estimated to be 2.96 mg cm2.

3. RESULTS AND DISCUSSION

3.1 XRD Analysis

Fig. 1a shows the results of an XRD measurement of the crystal structure of the assynthesized products. The purity of the ingredients used in the as-made goods, such as MnO2 (JCPDS no. 44-0141) and (JCPDS no. 20-0781), is easily verified. The peaks of MnO₂ and NiCo₂O₄ for the as-synthesized hybrid structures are also visible in the XRD data, suggesting that the MnO₂ and NiCo₂O₄ hybrid structures were successfully prepared.

The MnO_2 (JCPDS File No. 72-1982) peaks at 12.7° are indexed to the (110), respectively confirms the presence of MnO_2 in the prepared sample. Meanwhile, the peaks at 18.29, 30.35, 35.73, 43.4° are located on the (011), (020), (121), and (022) planes of NiCo₂O₄, respectively.

Data confirm the presence of MnO_2 and $NiCo_2O_4$. Good crystallinity has been achieved in the as-synthesized products, as seen by the sharp peaks. The simulated structure of $NiCo_2O_4@MnO_2$ was shown in Fig. 1b[26-28].



Figure 1: (a) XRD pattern of NiCo₂O₄ and NiCo₂O₄@MnO₂;(b) crystal structure of NiCo₂O₄

3.2 SEM Analysis

SEM and TEM are used to investigate the as-synthesized products' morphologies and microstructures. NiCo₂O₄ products as produced in SEM in Fig. 2a. In Fig.2b, we see the as-prepared NiCo₂O₄ products, which contain several nanosheets. NiCo₂O₄ structures, as synthesised, are uniformly coated on the surface of MnO₂ nanosheets (Fig. 2c).



Figure 2: (a,b) SEM images of NiCo₂O₄;(c,d) NiCo₂O₄@MnO₂;(e-g) Low magnification TEM images of NiCo₂O₄@MnO₂

In addition, as illustrated in Fig. 2d, the MnO_2 sheets are covered by an ultrathin $NiCo_2O_4$ sheet, with an average thickness of 30 nm. The microstructures of the synthesised goods are studied further using transmission electron microscopy (TEM). A low magnification TEM image of the MnO_2 @ $NiCo_2O_4$ hybrid structure is shown in Fig. 2e, confirming that $NiCo_2O_4$ nanosheets cover the surface of MnO_2 .

The (200) plane of MnO_2 and the (111) plane of $NiCo_2O_4$ may be distinguished in the HRTEM image of Fig. 2f, which exhibits two sets of lattice fringes with interplanar spacings of 0.486 nm and 0.468 nm, respectively. The Fig. 2f displays the lattice fringes of the MnO_2 (Zone II) hybrid structure, demonstrating the polycrystalline character of the as-obtained hybrid structures[29-30].

3.3 BET Analysis

Fig. 3(a,b) displays the nitrogen adsorption/desorption curves utilized to examine the specific surface areas and pore size distribution of NiCo₂O₄ and NiCo₂O₄@MnO₂ samples[31]. The adsorption/desorption isotherms of type II seen in the curves of the NiCo₂O₄ and NiCo₂O₄@MnO₂ samples indicate that both samples can be classified as mesoporous materials. The specific surface area of the NiCo₂O₄ @MnO₂ sample is seen to be 553.29 m² g-1, which is much higher than the specific surface area of the NiCo₂O₄ sample (380.58 m² g-1).

This discrepancy suggests that the introduction of N atoms through doping has resulted in an increase in the surface area. Furthermore, a distinct observation can be made from the inset of Figure 3 a,b indicating that the pore diameter distribution of the NiCo₂O₄@MnO₂ product exhibits a higher level of quality compared to that of the NiCo₂O₄ sample. The presence of a large surface area and an appropriate pore structure is advantageous for facilitating rapid electron and ion transport, as well as promoting the infiltration of electrolyte during electrochemical reactions.



Figure 3: (a) BET analysis of NiCo₂O₄(inset pore size distribution);(b) NiCo₂O₄@MnO₂ (inset pore size distribution)

3.4 XPS Analysis

As shown in Fig. 4, the as-synthesized MnO2@NiCo₂O₄ hybrid structures are subjected to an X-ray photoelectron spectroscopy (XPS) test to further investigate their surface chemical composition and the chemical valence of various elements. Two spin-orbit doublets and two shakeup satellites (named Sat.) suit the Ni 2p emission spectra very well.27,28. The two shakeup satellites are responsible for the fitting peaks at binding energies of 854.1 and 873.1 eV, respectively[32]. As seen in Fig. 4a, the presence of the satellite peak indicates that Ni mostly resides in the Ni2+ form. Co 2p's binding energy is between 780.2 and 795.2 eV, and its spectrum, as shown in Fig. 4b, fits into two spin-orbit doublets and satellite peaks: a low energy band (Co 2p 3/2) and a high energy band (Co 2p 1/2).

 Co^{2+} and Co^3 are present in the as-synthesized products, providing further confirmation of their presence. In this case, the weak satellite peak indicates that the majority of the Co is in the Co^{3+} state. Figure 1d depicts the fitting of the Mn 2p 3/2 spectrum into the three typical peaks of Mn²⁺, Mn³⁺, and Mn⁴⁺, with binding energies of 644.1, 642.0, and 642.0 eV, respectively with Mn⁴⁺ and Mn³⁺ being the major valence states. The Mn⁴⁺ ion has exceptional oxidation-reduction capability, while the Mn³⁺ ion occupies an intermediate valence and can be readily reduced to Mn⁴⁺ [33]



Figure 4: XPS analysis (a) Ni2p;(b) Co2p;(c) O1s;(d) Mn2p

3.5 Electrochemical Analysis

First, cyclic voltammogram (CV) measurements were performed in a three-electrode configuration with a Pt plate counter electrode and a AgCl reference electrode in 1 M KOH aqueous electrolyte on the as-synthesized hierarchical mesoporous NiCo₂O₄ @MnO₂ and NiCo₂O₄ nanosheets. NiCo₂O₄ were scanned at 5, 10, 20, and 50 mV s⁻¹ to get the CV curves shown in Fig. 5a. The as-prepared electrode materials are pseudocapacitive, as evidenced by the presence of a few redox peaks within the potential windows spanning 0 to 0.6 V, with these peaks primarily resulting from redox reactions related to M-O/M-O-ON, where M represents Ni, Co, or Mn ions and N represents H or K ions[34]. Curiously, the redox current grew as the scan rate got faster.

The oxidation and reduction peaks were likewise significantly separated in potential, with the former shifting towards higher potential and the latter towards lower potential. It is believed that the average area of the CV curve can be used to measure the specific capacitance of the electrode material. Fig. 4b displays the CV curves of NiCo₂O₄@MnO₂ electrodes.

Notably, the CV integrated area of the NiCo₂O₄@MnO₂ electrode materials appears to be larger than that of the pure NiCo₂O₄ electrode materials, indicating that the NiCo₂O₄@MnO₂ electrode materials have a significantly larger specific capacitance than unitary NiCo₂O₄ electrode materials. Further confirmation that the NiCo₂O₄@MnO₂ electrode materials have better electrochemical performance was provided by galvanostatic charge-discharge (CD) experiments at varying current densities.

At a current density 1, 3, 5,7,10 Ag⁻¹, Fig. 4c,d displays the GCD curves for the N NiCo₂O₄ and NiCo₂O₄@MnO₂ electrodes. The NiCo₂O₄@MnO₂ electrode, as predicted, has a significantly longer discharge time compared to the NiCo₂O₄ electrode. That's because the specific capacitance values displayed by the NiCo₂O₄@MnO₂ electrode material are greater than those displayed by the NiCo₂O₄ electrode material.

Typical results are displayed in Fig. 4e, and the Specific capacitances of NiCo2O4 and NiCo₂O₄@MnO₂ electrode materials were calculated based on their matching CD curves . Similarly, Fig. 4e analyses and plots the specific capacitance of NiCo₂O₄@MnO₂ electrode material at different current densities. While the NiCo₂O₄ nanowires only show a specific capacitance of 786, 710, 624, 542, 319, at 1, 3, 5,7,10 Ag⁻¹ the NiCo₂O₄@MnO₂ have specific capacitances up to 1215, 1056, 929, 763, 647 Fg⁻¹ at 1, 3, 5,7,10 Ag⁻¹.

We found that the NiCo₂O₄@MnO₂ electrode material had significantly higher electrochemical performance than other hybrid nanostructures, shown in table 1[35-42].

Asymmetric super capacitors	Electrolyte	Specific capacitance (F g-1)	Working potential (V)	Maximum energy density (Wh kg-1)	Maximum power density (kW kg-1)	Capacitance retention	Ref
Co3O4@ CoMoO4//CNTs	PVA/KOH	128	1.6	45.2	6.4	98.5 % after 3000 cycles	[35]
NiCo2O4/CC//PGP	PVA/LiOH	71.32	1.8	60.9	11.36	96.8% after 5000 cycles	[36]
Co3O4-NF//CA	PVA/KOH	57.4	1.5	17.9	7.5	85% after 1000 cycles	[37]
Al@Ni@MnOx// CCG PVA/ Na2SO4 58.78 1.8 23.02 0.947 96.3% after 10000 cycles [41]	PVA/ Na2SO4	58.78	1.8	23.02	0.947	96.3% after 10000 cycles	[38]
MnCo2O4@ Ni(OH)2//AC	2M KOH	141	1.6	48	14.9	90% after 2500 cycles	[39]
NiCo2O4@MnO2 //AC	1М КОН	120.9	1.5	37.8	7.5	98.38% after 3000 cycles	[40]
Co–Ni-DH// FeOOH	ЗМ КОН -		1.3	86.4	1.83	92.3% after 3000 cycles	[41]
Fe2O3@PPy// MnO2 0	.5 M Na2SO4	37.4	1.8	42.4	19.4	97.1% after 3000 cycles	[42]
NiCo ₂ O ₄ @MnO ₂ //AC	KOH/PVA	269	1.8	49.3	20.2	95% after 10,000 cycles	This Work

Table 1: Comparison with the previous work



Figure 5: Electrochemical analysis (a,b) CV spectrum of NiCo₂O₄, NiCo₂O₄@MnO₂; (c,d) GCD pattern of NiCo₂O₄, NiCo₂O₄@MnO₂; (e) Current density vs Specific capacitance Fg⁻¹

Electrochemical impedance spectroscopy (EIS) (Fig. 6a) also demonstrates the NiCo₂O₄@MnO₂ nanowires' remarkable performance increase. NiCo₂O₄@MnO₂ have a substantially lower equivalent series resistance (ESR; 0.9 U) than the naked NiCo₂O₄ nanowires electrode (1.5 U), indicating a reduced diffusion resistance.

For many real-world uses, the cycling performance of the supercapacitors is crucial. The CV test was run at a scan rate of 50 mV s1 for 10,000 cycles to determine the long-term cycle stability of the as-synthesized products as an electrode material (Fig. 6a,b). The specific capacitance retention of these two electrode materials is shown to first grow and then slightly decrease with time. This suggests that the electrodes undergo some sort of activation procedure at the outset of the CV cycling test.



Figure 6: (a) EIS spectrum of NiCo₂O₄, NiCo₂O₄@MnO₂;(b) Cyclic performance of NiCo₂O₄, NiCo₂O₄@MnO₂; Capacity contribution performance of NiCo₂O₄@MnO₂

In this procedure, ions will intercalate and de-intercalate at the electrode, resulting in an increase in active spots within the electrode materials and a corresponding rise in the specific capacitance. Overall, the NiCo₂O₄@MnO₂ electrode material retains 98% of its specific capacitance after 10,000 cycles, while the NiCo₂O₄ electrode material retains 92% of its capacitance after the same number of cycles. NiCo₂O₄@MnO₂ electrodes' superior pseudocapacitive performances can be traced back to their distinctive mesoporous structure, which provides more active sites for efficient electrolyte ion transportation not only at the active materials' surface but also in the bulk.

Hierarchical mesoporous NiCo₂O₄@MnO₂ nanosheet arrays on have a number of advantages that contribute to their high performance, such as: To get around the low conductivity of MnO₂ nanosheets, (i) mesoporous NiCo₂O₄ nanosheets with good electrical conductivity produced directly on nickel foam will provide electron "superhighways" for charge storage and transport. (ii) The mesoporous structures can reduce the ion transport resistance by acting as an "ion reservoir," which will greatly improve the intercalation/deintercalation of ions and the utilisation rate of electrode

materials even at high current densities, thanks to the shorter diffusion distance from the external electrolyte to the interior surfaces, (iii) A material combination, such as NiCo₂O₄ and MnO₂, will yield synergistic and multifunctional effect. It is possible to avoid "dead" volume produced by the time-consuming procedure of mixing active materials with polymer binders/conductive additives by directly growing hierarchical mesoporous NiCo₂O₄@MnO₂ nanosheet arrays.

3.6 Electrochemical Analysis of Fabricated NiCo₂O₄@MnO₂//AC

NiCo₂O₄ @ MnO₂ was used as the positive electrode and porous carbon was used as the negative electrode in an aqueous 3 M KOH asymmetric supercapacitor (ASC). The constructed supercapacitor can supply an operational potential of 0-1.50 V in 3 M KOH, as shown by the potential windows of NiCo₂O₄ @ MnO₂ and porous carbon, respectively, which are 0 to 0.5 V and 1.0 to 0 V. As can be shown in Fig. 7a, the ASC device maintains a constant 1.5 V over its large operating voltage. Capacitances of 114, 104, 94, 85, and 77 F g1 were measured at 1, 2, 3, 4, and 5 A g1 current densities in NiCo₂O₄ @ MnO₂ //C, as shown in the GCD curves in Figure 7b. Figure 7c depicts the rate performance of the NiCo₂O₄ @ MnO₂ //C asymmetric supercapacitor device.



Figure 7: (a) CV spectrum of NiCo₂O₄@MnO₂//AC; (b) GCD pattern of NiCo₂O₄@MnO₂//AC (c) Cyclic performance of NiCo₂O₄@MnO₂//AC; (d) Specific capacitance Fg⁻¹ vs Current Density Ag⁻¹ of NiCo₂O₄@MnO₂//AC

Fig 8a shows the Schematic showing of fabricated devices capacitor. For supercapacitors to be used in everyday situations, energy density and power density must be high. Fig. 8b displays Ragone plots (energy density against power density).

In order to determine the ASC's power density and energy density, the following equations were used:



Figure 8: (a) Schematic showing of fabricated asymmetric capacitor;(b) Ragone Plot

At a power density of 20 kW kg1, the NiCo₂O₄ @ MnO₂ //C asymmetric supercapacitor has a high energy density of 49.6 Wh kg1. Energy density remains unchanged at 52 Wh kg1 when the current density is increased to 5 A g1, while power density can reach 15 kW kg1. The figure also reveals that the curve is reasonably steady, with no sudden dips. Therefore, high-energy-density storage is a possible use for the NiCo₂O₄ @ MnO₂ //C asymmetric supercapacitor. As can be seen in Fig. 7d, the NiCo₂O₄ @ MnO₂ //C asymmetric supercapacitor underwent a cycling stability test at a current density of 5 A g1. The cycling performance of the asymmetrical supercapacitor is consistent and free of significant fluctuations. The ASC's specific capacitance maintains 90% of its initial value after 10,000 cycles. These findings show that the ASC performs well and has real-world applications in high-density energy storage.

CONCLUSION

In summary, this study presents an all-solid-state asymmetric supercapacitor configuration that utilizes a unique nanosheet heterostructure of NiCo₂O₄ @ MnO₂ as the positive electrode, a three-dimensional network of Activated Carbon as the negative electrode, and PVA/KOH as the electrolyte. The experimental results demonstrate the superior performance of this configuration, including a high-rate capacitance, excellent cycling stability for over 10,000 cycles, a maximum energy density of 49.2 Wh kg-1, a maximum power density of 20.3 kW kg-1, and an extended high operating range of 1.8 V. The exceptional electrochemical capabilities of the asymmetric supercapacitor can be attributed to the unique three-dimensional nanostructure characteristics exhibited by the positive and negative electrode materials. The NiCo₂O₄ @ MnO₂ heterostructure exhibits exceptional properties such as structural stability, efficient electron/ion transportation, and remarkable pseudo-

capacitive behavior. These attributes are attributed to the synergistic impact resulting from the combination of MnO2 and NiCo₂O₄ nanosheets during electrochemical reactions. Furthermore, the exceptional rate and cycle capabilities seen in the asymmetric supercapacitor can be attributed to the notable characteristics of the ultrathin nanosheets, including their high electron conductivity, substantial surface area, and favourable pore structure. Hence, we suggest that the research technique holds great potential for the development of advanced energy storage devices in the field of energy-power technology.

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