



# Flower like NiCo<sub>2</sub>O<sub>4</sub>@NiMoO<sub>4</sub> Heterostructure Enabling Enhanced Electrochemical Performance for Supercapacitor Electrodes

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## Abstract

A novel electrode material of the three-dimensional (3D) multicomponent oxide of Nickel Cobaltite and Nickel Molybdate heterostructures (NiCo<sub>2</sub>O<sub>4</sub>@NiMoO<sub>4</sub>) has been synthesized by a facile microwave irradiation method, and an X-ray diffractogram (XRD) measurement confirms the materials' crystalline phase. A surface composition analysis using XPS was conducted. NiCo<sub>2</sub>O<sub>4</sub>, NiMoO<sub>4</sub> and NiCo<sub>2</sub>O<sub>4</sub>@NiMoO<sub>4</sub> has a structure resembling a nanoplate, nanosheet, and coreshell, as demonstrated by HR-SEM and TEM investigation. For NiCo<sub>2</sub>O<sub>4</sub>, electrochemical tests revealed pseudocapacitive behavior. Among all NiCo<sub>2</sub>O<sub>4</sub>@NiMoO<sub>4</sub> displayed excellent supercapacitor performance with a high specific capacitance of 2724 F g<sup>-1</sup> at 1 Ag<sup>-1</sup> and high energy density of 83.5 Wh kg<sup>-1</sup> with catalytic stability.

**Keywords:** Heterostructure, specific capacitance, supercapacitor, power density, energy density, microwave heating.

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## 1. Introduction

Energy storage technologies with high performance, low cost, and environmental friendliness have received a lot of attention in recent years from both the industrial and academic worlds [1-3] due to the continuously growing demand for green energy. Researchers are investigating several electrode materials because supercapacitor components are more affordable and less dangerous. However, because to their low energy densities, for which battery-type electrodes are currently preferred, supercapacitors have a restricted range of practical applications. As electrode materials for supercapacitors, a variety of transition mono-/multi-metallic oxides or hydroxides have been studied [4,5]. The electrode materials used in supercapacitors can be divided into two groups based on the various energy storage processes: electric double-layer capacitors (EDLCS) and pseudo capacitors (PCS) [6]. In

comparison to EDLCs, PCS have significantly greater capacitance values and energy densities due to their rapid and reversible redox reaction [7].

The hydrothermal method is one of the more traditional ways to create different nanomaterials among the numerous synthesis procedures. It's interesting that several nanomaterials with varying dimensions, dopants, core-shell configurations, heterostructures, etc. have been discovered to be effective for energy storage applications [8,9]. Due to its high theoretical capacitance, low cost, abundance, and environmental friendliness, nickel-cobalt metal oxide has received a great deal of study attention. Additionally, it is anticipated to offer richer redox reactions than the two comparable single-component oxides, incorporating contributions from both nickel and cobalt oxides [10]. However, due to their low electrical conductivity and small surface area, transition metal oxides, such as NiCo<sub>2</sub>O<sub>4</sub>, typically exhibit restricted kinetics during the redox reaction [11]. Interestingly, metal molybdates as NiMoO<sub>4</sub> have a low rate performance despite having a high specific capacitance due to the strong electrochemical activity of nickel ions.

When compared to pure NiCo<sub>2</sub>O<sub>4</sub>, hetero-nanostructured NiCo<sub>2</sub>O<sub>4</sub>@NiCo<sub>2</sub>O<sub>4</sub> and NiCo<sub>2</sub>O<sub>4</sub>@NiO at 0.5 A g<sup>-1</sup> exhibit superior cycling stability, good rate capability, and high specific capacitance of 1925 and 2210 F g<sup>-1</sup>, respectively. These materials exhibit excellent electrochemical performance [13]. The spinel nickel cobaltite (NiCo<sub>2</sub>O<sub>4</sub>), one of the ternary metal oxides (TMOs), has one of the highest theoretical specific capacitances, the best electrical conductivity, and the highest electrochemical activity [14]. The synthetic composite had a high specific capacitance of 2220 F g<sup>-1</sup> at 1 A g<sup>-1</sup> and demonstrated improved faradic behavior. Simple solvothermal synthesis produced a nickel foam supported NiO@NiCo<sub>2</sub>O<sub>4</sub>, with a significant specific capacitance of 1623.6 F g<sup>-1</sup> at 2 A g<sup>-1</sup>[15].

Jiang et al. created NiMoO<sub>4</sub> nanoclusters with one-dimensional nanorods using a simple microwave-assisted technique, and they demonstrated a capacitance of 680 F g<sup>-1</sup> at 1 A g<sup>-1</sup> [16]. According to Mai et al., the hierarchical-pore nanowires of heterostructured MnMoO<sub>4</sub>/CoMoO<sub>4</sub> are superior to the mono-metal oxide of MnO<sub>2</sub> or Co<sub>3</sub>O<sub>4</sub>, having a specific capacitance of 187.1 F g<sup>-1</sup> at a current density of 1 A g<sup>-1</sup> and a cycling efficiency of 98% after 1,000 cycles [17]. However, due to the poor conductivities of pure NiMoO<sub>4</sub>, which limit their practical applicability, the specific capacitances of NiMoO<sub>4</sub>-related materials are significantly lower than their theoretical values. Due to their synergistic effects, an array of heterostructured materials demonstrated better electrochemical performance [18].

Microwave heating (MWH) is a synthesis technique that has the advantages of rapid heating and high reaction rates, as well as low energy consumption, high heating efficiency, and much shorter reaction times. As a result, the cost of finished products can be reduced [19,20]. Additional benefits of MWH include its excellent selectivity, homogenous volumetric heating, and high microwave penetration depth.

In the current work, a unique NiCo<sub>2</sub>O<sub>4</sub>@NiMoO<sub>4</sub> core-shell electrode material was created using the microwave oven approach. Since NiMoO<sub>4</sub> and NiCo<sub>2</sub>O<sub>4</sub> are both promising candidate materials for supercapacitors on their own, the combination of the two materials to form a complex core-shell structure is anticipated to significantly increase the surface area to provide more electroactive sites for Faradaic reactions and create quick pathways for electrolytic ions and electron diffusion and transportation, as well as to enable synergistic

effects of NiCo<sub>2</sub>O<sub>4</sub> and NiMoO<sub>4</sub> to increase the capacity of the super simple microwave irradiation significantly was used to create the heterostructures. In order to create the core-shell heterostructure, the NiMoO<sub>4</sub> nano species is deposited outside of the NiCo<sub>2</sub>O<sub>4</sub> nanoparticles. As a result, a two-step strategy involving microwave synthesis and calcination was suggested. The "core" was made of NiCo<sub>2</sub>O<sub>4</sub>, and the "shell" was made of NiMoO<sub>4</sub>.

## 2. Experimental Analysis

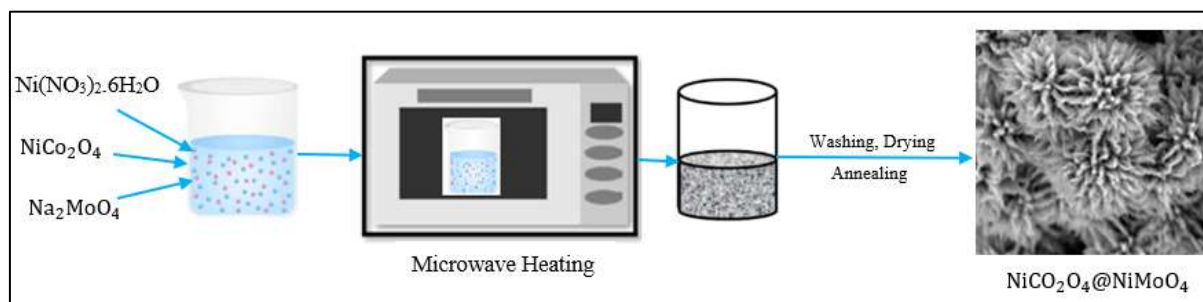
Nanomaterials of NiCo<sub>2</sub>O<sub>4</sub>@NiMoO<sub>4</sub> were synthesized by facile microwave irradiation method.

### 2.1 Synthesis of NiCo<sub>2</sub>O<sub>4</sub>

For the synthesis of NiCo<sub>2</sub>O<sub>4</sub>, initially, nickel nitrate hexahydrate and cobalt nitrate hexahydrate were taken in 1:2 weight ratio and the precursors were dissolved in the mixture of distilled water and ethanol (40 ml: 40ml). A homogenous Ni – Co precursor solution was obtained after the vigorous stirring for 30 min. The required amount of NaOH pellets were introduced to the above solution with continuous stirring for 30 min. The resultant solution was kept in the LG microwave oven (MH-4048 GW) to undergo microwave irradiation. The output power was maintained as 800 W with an operating frequency of 2.45 GHz. The irradiation was continued for 5 min and then it was left to cool down to the ambient temperature. The obtained product was subjected to wash with double distilled water and ethanol to remove the ions and byproducts. In order to dry, the product was kept in a hot-air oven at 60°C for 12 h. The dried product was mixed 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 Synthesis of NiCo<sub>2</sub>O<sub>4</sub>@NiMoO<sub>4</sub>

The NiMoO<sub>4</sub> was grown on the prepared NiCo<sub>2</sub>O<sub>4</sub> to form the NiCo<sub>2</sub>O<sub>4</sub>@NiMoO<sub>4</sub> material also by a microwave heating method. 0.25g of freshly prepared NiCo<sub>2</sub>O<sub>4</sub> was added to 80 ml of Distilled water in a clean beaker. Now add 1.164 g of Nickel (II) Nitrate Hexa hydrate Ni(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O to the above solution and stir for 20-30 mts. Now add 0.823g of Sodium Molybdate Hepta Hydrate Na<sub>2</sub>MoO<sub>4</sub>. to the above solution again stir well for 20-30 min using a magnetic stirrer for obtaining a homogenous solution. The final solution was transferred into a clean thick glassed beaker kept in a household microwave oven (2.45 GHz) with power up to 1 kW and irradiated for 2,3,5 till 8 minutes in steps with the ON/OFF conditions to avoid overheating. After cooling down to room temperature, the products were taken out and rinsed with deionized water and ethanol for 2-3 times, then dried at 60°C for 3 h. Then the remaining synthesis procedure such as the microwave process, drying and annealing at 350°C in air for 2 h were followed as similar to the procedure which was followed for the NiCo<sub>2</sub>O<sub>4</sub> synthesis. Schematic representation of the synthesis process of NiCo<sub>2</sub>O<sub>4</sub>@NiMoO<sub>4</sub> is shown in Fig. 1.



**Fig.1.** Synthesis scheme of NiCo<sub>2</sub>O<sub>4</sub>@NiMoO<sub>4</sub>

## 2.3 Characterizations techniques

Powder X-ray diffraction (XRD) analysis was done using PANalytical, Netherlands, using Cu –  $K\alpha$  radiation in the  $2\theta$  range from  $10^\circ$  to  $80^\circ$  to evaluate the crystalline phase of the produced materials. X-ray photoelectron spectroscopy (XPS, PHI Versa probe III) with Al $K\alpha$  monochromatic radiation analysis was used to evaluate the surface elemental compositions. The surface morphology and nanostructures of the prepared materials were photographed using a High-Resolution Scanning Electron Microscope (HR-SEM) and a High-Resolution Transmission Electron Microscope (HR-TEM) using Thermo scientific Apreo S, JEOL Japan and JEM-2100 Plus, respectively. The electrochemical performance was further explored using galvanostatic charge-discharge measurements.

## 2.4 Electrochemical measurements

The three-electrode system, which includes active material coated nickel foam, silver/silver chloride, and platinum wire as working electrodes, references, and counter electrodes, was used to study the electrochemical properties. To remove the electrode's surface particles,  $2 \times 1$  cm of nickel foam was taken and sonicated with ethanol and acetone for a short period of time. In order to create the working electrode, first 85 wt.% of the active material, 10 wt.% of carbon black, and 5 wt.% of polyvinylidene fluoride (PVDF) were thoroughly mashed in a mortar pestle and made slurry by introducing few drops of N-Methyl-2-pyrrolidinone with the above mixture. The resultant slurry was coated uniformly at  $1 \times 1$  cm on a pre-treated Ni foam, and it was then dried at  $60^\circ\text{C}$  for 24 hours. Using a Bio-Logic SP 300 (France) electrochemical workstation, the constructed electrodes were tested for electrochemical performance in a 1 M KOH electrolyte solution. The following equation is used to compute the specific capacitance:

$$C_s = \frac{I\Delta t}{m\Delta V}$$

where  $I$  (A) represents the discharge current,  $C$  ( $\text{Fg}^{-1}$ ) is the specific capacitance, and  $m$  (mg),  $\Delta V$  (V), and  $\Delta t$  (s) designate the mass of active materials, potential drop during discharge, and total discharge time respectively.

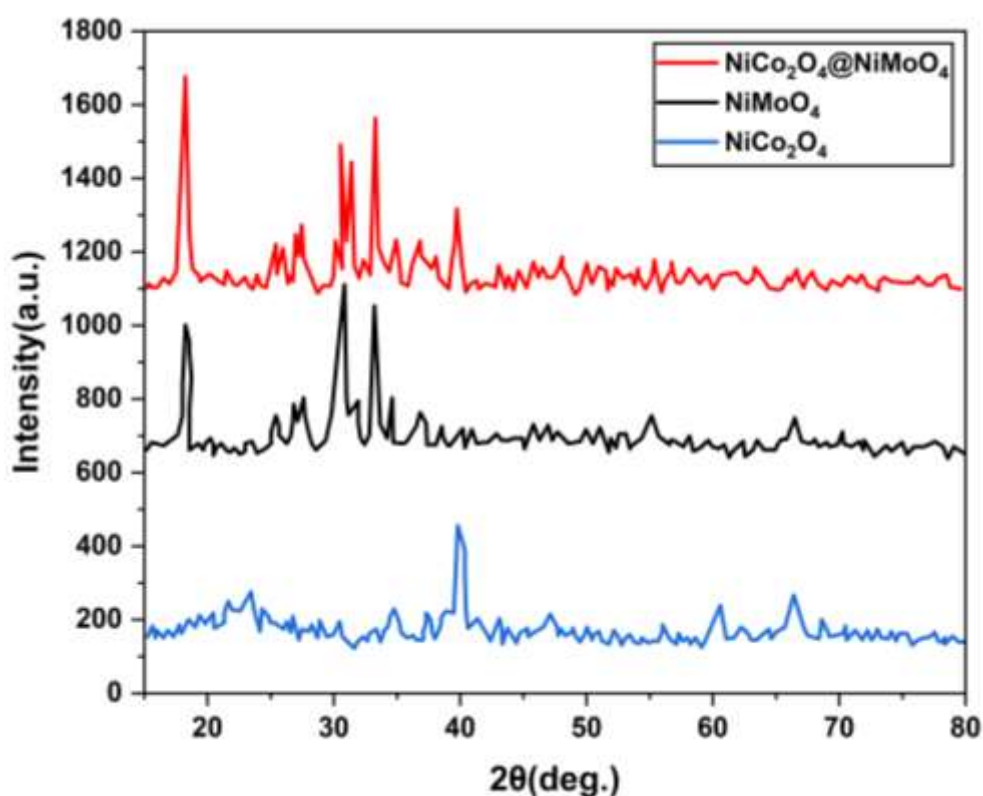
### 3. Results and discussion

#### 3.1 Formation mechanism of NiCo<sub>2</sub>O<sub>4</sub>@NiMoO<sub>4</sub> core-shell nanomaterials

The formation mechanism of NiCo<sub>2</sub>O<sub>4</sub>@NiMoO<sub>4</sub> core-shell nanomaterials is proposed by facile microwave irradiation method. Nano-NiCo<sub>2</sub>O<sub>4</sub> cores were first created. Then to create the final hierarchical NiCo<sub>2</sub>O<sub>4</sub>@NiMoO<sub>4</sub> core shell nanomaterials, a thin coating of NiMoO<sub>4</sub> was deposited onto the surface of the NiCo<sub>2</sub>O<sub>4</sub> cores.

#### 3.2 XRD analysis

The XRD analysis was used to examine the crystal structures of NiCo<sub>2</sub>O<sub>4</sub>, NiMoO<sub>4</sub> and NiCo<sub>2</sub>O<sub>4</sub>@NiMoO<sub>4</sub> as they were produced. NiCo<sub>2</sub>O<sub>4</sub>@NiMoO<sub>4</sub> reaches its maximum peak at 1750 at intensity a.u. at 27.6 (2 $\theta$  deg.) as shown in Fig. 2. The (111), (220), (311), (222), (400), (422), (511) and (440) crystal planes of NiCo<sub>2</sub>O<sub>4</sub> can be indexed as the diffraction peaks at 19.2, 31.4, 35.8, 36.8, 39.7, 46.3, 56.8, 60.4, 67.2° (JCPDS card no. 73-1702). The low crystallinity of the pure NiCo<sub>2</sub>O<sub>4</sub> is indicated by the large diffraction peaks. The standard patterns for NiMoO<sub>4</sub> · xH<sub>2</sub>O (JCPDS, card no. 13-0128) and the patterns of single NiMoO<sub>4</sub> are in remarkable accord. NiMoO<sub>4</sub> impurity phase was also linked to a number of diffraction peaks (JCPDS, card no. 12-0348). The pattern of NiCo<sub>2</sub>O<sub>4</sub>@NiMoO<sub>4</sub> contains the peaks of NiCo<sub>2</sub>O<sub>4</sub>@NiMoO<sub>4</sub> (JCPDS, card no.12-0348), and NiMoO<sub>4</sub> · xH<sub>2</sub>O (JCPDS, card no.13-0128), showing that two phases of as-synthesized NiMoO<sub>4</sub> are coexisting on the surface of NiCo<sub>2</sub>O<sub>4</sub>. Because NiMoO<sub>4</sub> nanosheets wrap around the surface of the NiCo<sub>2</sub>O<sub>4</sub> nanostructure and cover NiCo<sub>2</sub>O<sub>4</sub> with strong diffraction peaks, the intensity of the diffraction peaks corresponding to NiCo<sub>2</sub>O<sub>4</sub> is reduced in the patterns of NiCo<sub>2</sub>O<sub>4</sub>@NiMoO<sub>4</sub> materials.



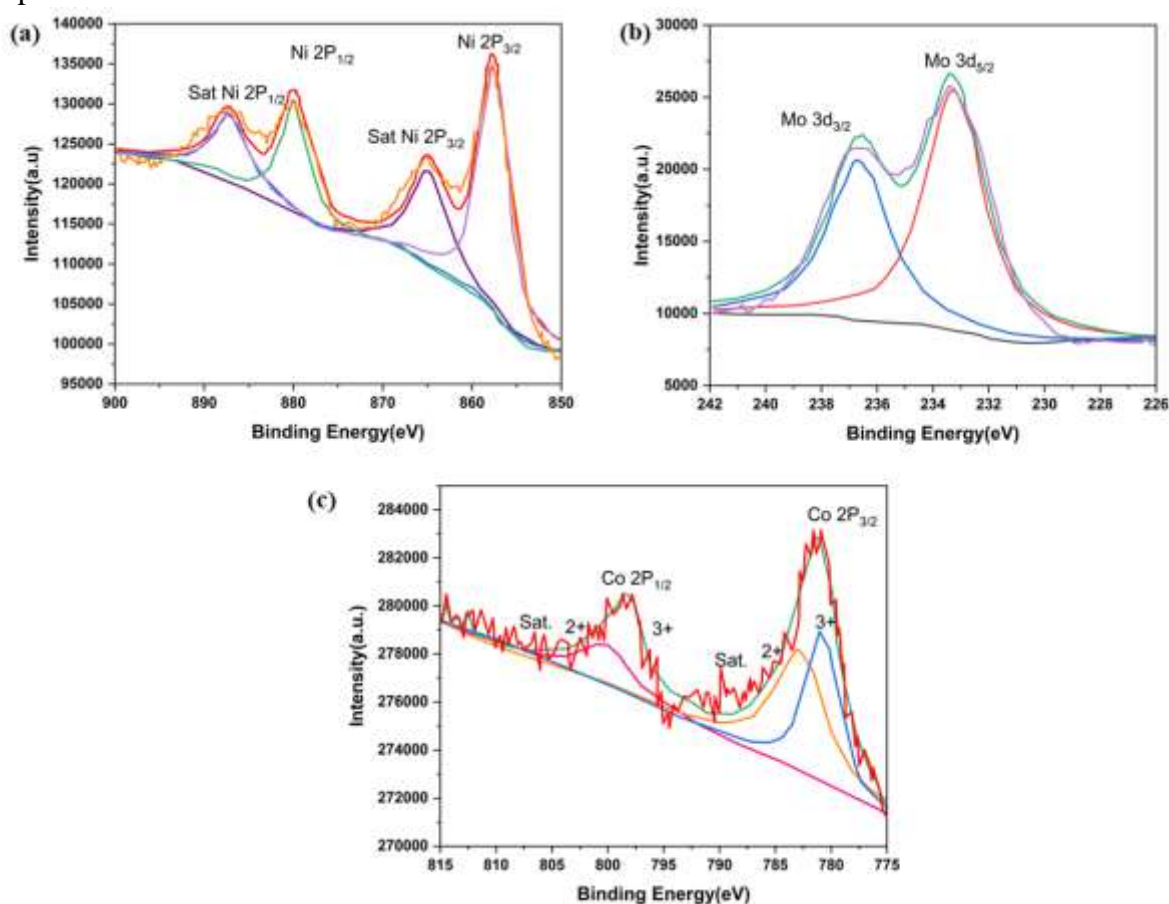
**Fig. 2.** XRD patterns of NiCo<sub>2</sub>O<sub>4</sub>@NiMoO<sub>4</sub>



### 3.3 XPS analysis

The elemental composition and oxidation state of NiCo<sub>2</sub>O<sub>4</sub>@NiMoO<sub>4</sub> as synthesized are further understood by XPS measurements, which show the presence of Ni, Mo, Co, and O as well as C from the reference and the absence of any other element. The Ni2p<sub>3/2</sub> level is represented by the binding energy peak at 857.4eV and its satellite peak at 864.8eV, whereas the Ni2p<sub>1/2</sub> level is represented by the binding energy peak at 881.7eV and its satellite peak at 887.3 eV as depicted in Fig. 3(a). Ni2p<sub>3/2</sub> and Ni2p<sub>1/2</sub> have major binding energy peaks that are 17.8eV apart from one another, which is a characteristic of the Ni<sup>2+</sup> oxidation state. The Mo 3d core level spectra (Fig. 3(b)) display two peaks for Mo 3d<sub>5/2</sub> and Mo 3d<sub>3/2</sub>, respectively, with binding energies of 232.8 eV and 236.9 eV. Mo 3d has binding energy peaks that are 3.1 eV apart, which also denotes a Mo(VI) oxidation state.

More specifically, Co<sup>2+</sup> is responsible for the fitting peaks at 783.4 eV and 797.5eV, the binding energies (EB) of Co(II) ions, whereas Co<sup>3+</sup> and two shake-up satellites (referred to as "Sat.") are responsible for the fitting peaks at 784.9 and 798.2 eV, as illustrated in Fig. 3(c). Three contributions from oxygen are visible in the high-resolution spectra of the O1s area. The peak at 530.2eV in particular, is typical of metal-oxygen bonding. The peak at 531.4eV is frequently linked to flaws, impurities, and various surface species, such as hydroxyls, chemisorbed oxygen, under-coordinated lattice oxygen, or species native to the spinel's surface.

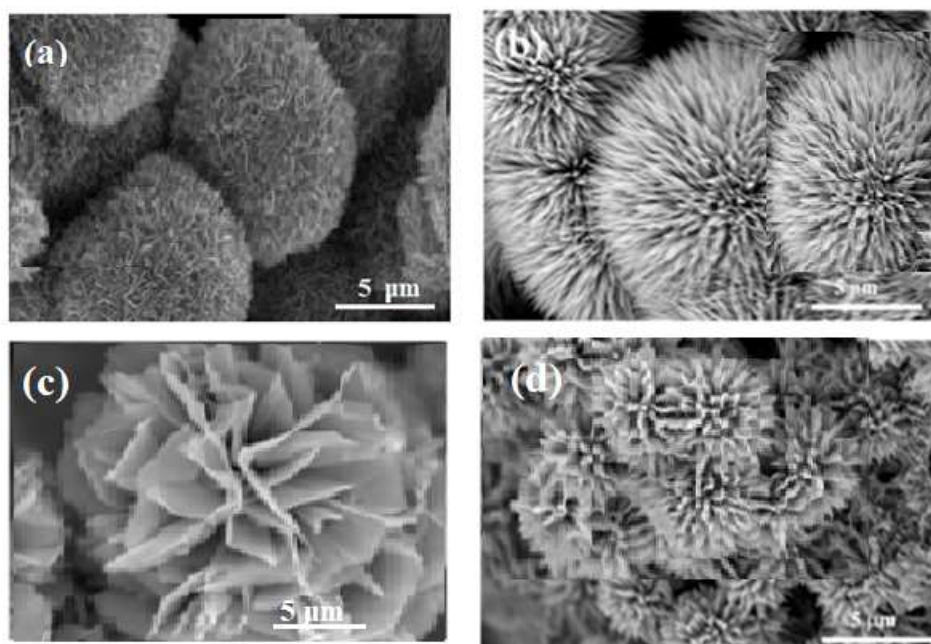


**Fig. 3.** XPS spectra (a)Ni 2p, (b) Co 2p and (c) Mo 3d for flower like NiCo<sub>2</sub>O<sub>4</sub>@NiMoO<sub>4</sub> microspheres

The plurality of physi- and chemisorbed water at or near the surface is the probable cause of the peaks at 532.6eV. These findings demonstrate that Ni<sup>2+</sup>, Ni<sup>3+</sup>, Mo(vr), Co<sup>2+</sup>, Co<sup>3+</sup> and O<sup>2-</sup>, are present in the surface composition of the as-synthesised NiCo<sub>2</sub>O<sub>4</sub>@NiMoO<sub>4</sub> material, which is in good accord with the findings of NiMoO<sub>4</sub> and NiCo<sub>2</sub>O<sub>4</sub> as core-shell structure: The "core" was made of NiCo<sub>2</sub>O<sub>4</sub>, and the "shell" was made of NiMoO<sub>4</sub>. It is obvious that it is made up of Ni, Co, Mo, and O elements. The parent hierarchical heterostructures are a mixture of NiCo<sub>2</sub>O<sub>4</sub> and NiMoO<sub>4</sub>, which is in good agreement with the XRD data, and the nanosheets that have formed on the surface are primarily made up of NiMoO<sub>4</sub>.

### 3.4 Morphological analysis

The morphologies of NiCo<sub>2</sub>O<sub>4</sub> and NiCo<sub>2</sub>O<sub>4</sub>@NiMoO<sub>4</sub> were studied by FESEM, as illustrated in Fig. 4. As seen in Fig. 4(a) the NiCo<sub>2</sub>O<sub>4</sub> material possesses a flower-like characteristic with a 5 μm diameter and sharp nano-needles. Fig 4(b) displays the SEM image of NiMoO<sub>4</sub>.

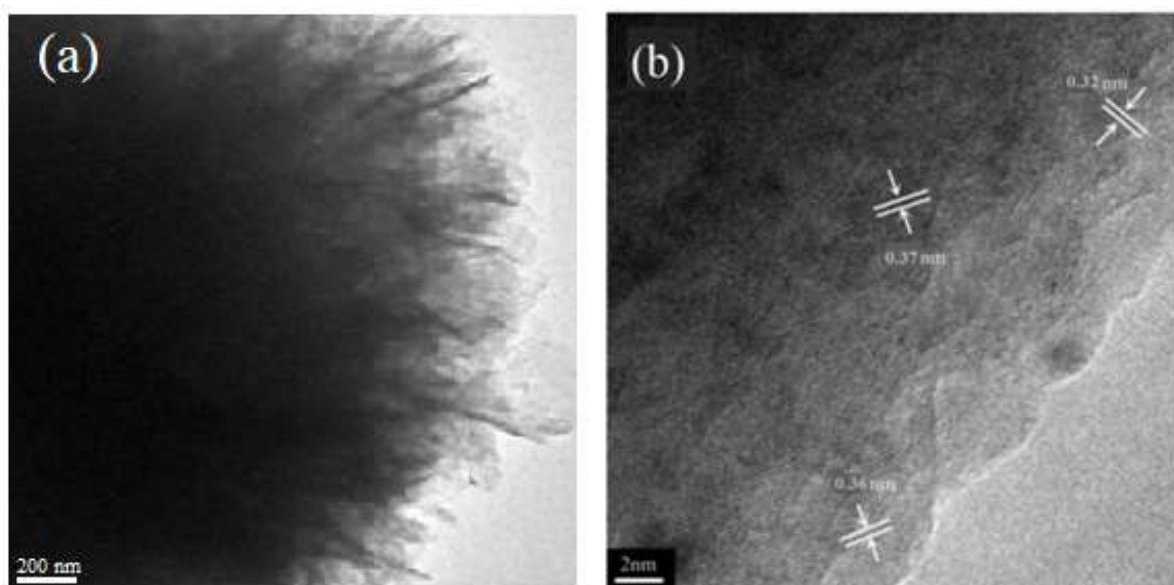


**Fig. 4.** (a) SEM image of the NiCo<sub>2</sub>O<sub>4</sub>; (b) SEM image of NiMoO<sub>4</sub>; (c, d) SEM images of core-shell NiCo<sub>2</sub>O<sub>4</sub>@NiMoO<sub>4</sub> nanostructures.

The SEM image of the NiCo<sub>2</sub>O<sub>4</sub>@NiMoO<sub>4</sub> core-shell material is shown in Fig. 4(c) and (d). However, the needles of NiCo<sub>2</sub>O<sub>4</sub> were uniformly wrapped by short NiMoO<sub>4</sub> nanorods to form a core-shell nanostructure, resulting in NiCo<sub>2</sub>O<sub>4</sub>@NiMoO<sub>4</sub> bristled nanorods of about 200 nm diameter. It is clear that the fundamental structure of NiCo<sub>2</sub>O<sub>4</sub> is still preserved. The

coated nanorods outside of the NiCo<sub>2</sub>O<sub>4</sub> needles also have a flower-like morphology, as seen in Fig. 4(d).

TEM and HRTEM are used to examine the morphology and structure of the NiCo<sub>2</sub>O<sub>4</sub> and NiCo<sub>2</sub>O<sub>4</sub>@NiMoO<sub>4</sub> core-shell nanomaterial in greater detail.



**Fig. 5.** (a) Low-magnification TEM image, (b) HRTEM image of the NiCo<sub>2</sub>O<sub>4</sub>@NiMoO<sub>4</sub> core-shell nanostructures

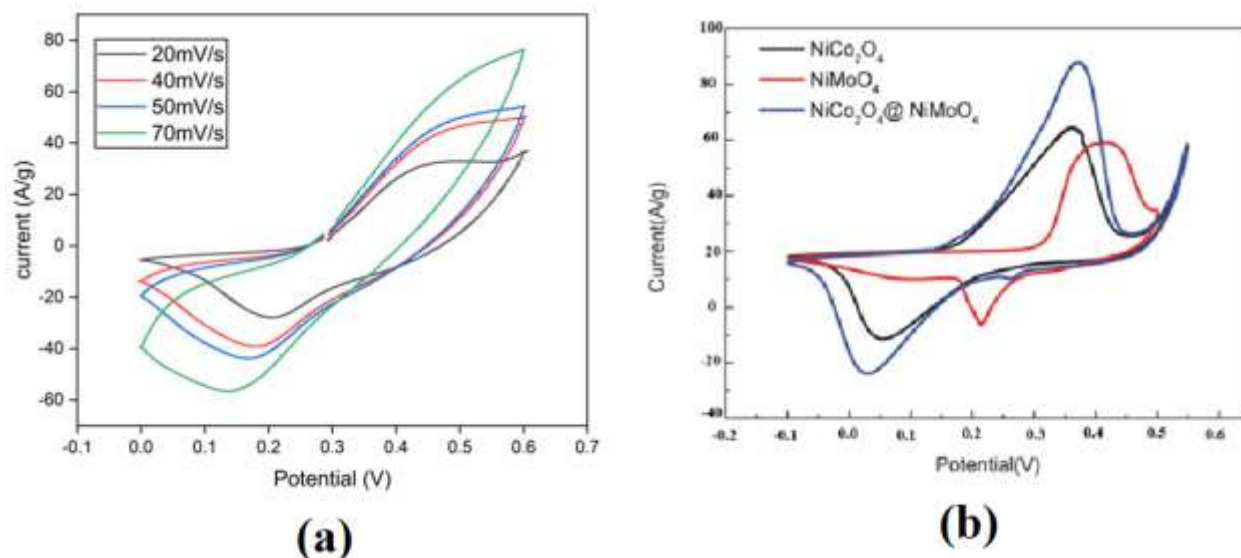
According to Fig. 5(a), NiCo<sub>2</sub>O<sub>4</sub> exhibits flower-like shape with pointed nanoneedles that radiate from the center of the ball. It is extremely compatible with FESEM findings. The high-resolution TEM (HRTEM) image reveals that the NiCo<sub>2</sub>O<sub>4</sub> (311) crystal plane's lattice spacing is 0.36 nm. Unfortunately, NiMoO<sub>4</sub>'s crystal structure is not well understood, therefore it is still unclear to which plane the measured gap belongs. The diameter of the nanorods NiCo<sub>2</sub>O<sub>4</sub>@NiMoO<sub>4</sub> (the edge of the dark image) is around 200 nm, which is in good agreement with that of SEM. Fig. 5(b) shows the HRTEM image of the NiMoO<sub>4</sub> shell. The lattice spacing of 0.32 nm is similar to that of 0.319 nm in the JCPDS 13-0128 file, while the interplanar spacings are 0.36 nm and 0.37 nm, respectively, which are comparable to the values of 0.365 nm and 0.37 nm provided in the JCPDS 12-0348 file. The NiCo<sub>2</sub>O<sub>4</sub>@NiMoO<sub>4</sub> material's high porosity and expansive surface are attributable to the hierarchical mesopores that are formed when NiMoO<sub>4</sub> nanorods assemble and aggregate on the NiCo<sub>2</sub>O<sub>4</sub> needles.

### 3.5 Electrochemical measurements

Pure NiCo<sub>2</sub>O<sub>4</sub> > NiMoO<sub>4</sub> is followed by NiCo<sub>2</sub>O<sub>4</sub>@NiMoO<sub>4</sub> in terms of integral CV area and height of oxidation peak, showing that the former electrode has a higher specific capacitance than the latter two. The increased electrochemical reaction activity of the core-shell nanoflake arrays may be attributed to the NiMoO<sub>4</sub> shell's enhanced contribution to the pseudocapacitance. As synthesized NiCo<sub>2</sub>O<sub>4</sub>@NiMoO<sub>4</sub> nanomaterials may be used in electrochemical supercapacitors because of their porous architectures and large surface areas,



which may help with ion transfer at the electrode/electrolyte interface. The area of the NiCo<sub>2</sub>O<sub>4</sub>@NiMoO<sub>4</sub> electrode, in contrast to that of NiMoO<sub>4</sub>, exhibits a clear rise on the left side of the redox peaks. NiCo<sub>2</sub>O<sub>4</sub> is the primary cause of this expanded area. This suggests that NiCo<sub>2</sub>O<sub>4</sub>@NiMoO<sub>4</sub> electrode materials perform better in supercapacitive applications when both NiMoO<sub>4</sub> and NiCo<sub>2</sub>O<sub>4</sub> are present.

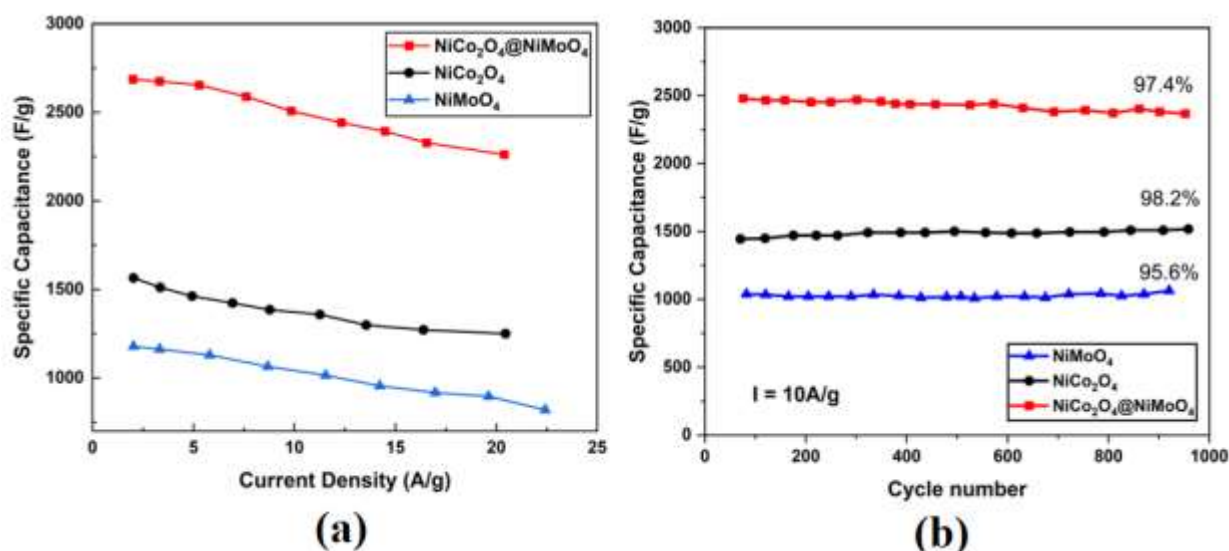


**Fig. 6** Electrochemical performances of NiCo<sub>2</sub>O<sub>4</sub>, NiMoO<sub>4</sub> and NiCo<sub>2</sub>O<sub>4</sub>@NiMoO<sub>4</sub> (a) CV curves at different scan rates for NiCo<sub>2</sub>O<sub>4</sub>@NiMoO<sub>4</sub> electrode; (b) comparative CV curves.

The NiCo<sub>2</sub>O<sub>4</sub>@NiMoO<sub>4</sub> electrode's CV curves are displayed in Fig. 6(a) at scan rates of 20, 40, 50, 70 mVs<sup>-1</sup> in the potential range of 0.0 to 0.6 V (vs. SCE). It is clear that the peak current increases as the scan rate rises, indicating that at the provided scan rates, the interfacial kinetics and rates of electronic and ionic transport are fast enough. The polarization action of the electrode is responsible for the anodic peaks shifting towards the positive potential and the cathodic peaks shifting towards the negative potential. The cyclic voltammetry (CV) curves of the NiCo<sub>2</sub>O<sub>4</sub>, NiMoO<sub>4</sub>, and NiCo<sub>2</sub>O<sub>4</sub>@NiMoO<sub>4</sub> electrodes are shown in Fig. 6(b) at a scan rate of 10mVs<sup>-1</sup>. The three electrodes clearly show a pair of redox peaks, specifically oxidation peaks at 0.35, 0.40, 0.36 V and reduction peaks at 0.04, 0.22, 0.03 V for NiCo<sub>2</sub>O<sub>4</sub>, NiMoO<sub>4</sub> and NiCo<sub>2</sub>O<sub>4</sub>@NiMoO<sub>4</sub>, respectively. These peaks are primarily attributed to the redox reactions of the Ni and Co species in the alkaline electrolyte.

During the procedure, a clear plateau region may be seen, pointing to the electrodes' pseudocapacitive activity. Fig. 7(a) displays the computed specific capacitances for the three electrodes at varying discharge current densities. The specific capacitance of NiCo<sub>2</sub>O<sub>4</sub>@NiMoO<sub>4</sub>(2724 Fg<sup>-1</sup>) is significantly higher than that of pure NiCo<sub>2</sub>O<sub>4</sub>(1685 Fg<sup>-1</sup>) and NiMoO<sub>4</sub>(1435 Fg<sup>-1</sup>) at a current density of 1 Ag<sup>-1</sup>. Even though there is insufficient active material involved in the redox reaction at high current densities and the specific capacitance gradually decreases with increasing current density due to the incremental voltage drop, the specific capacitance is still as high as 2428 Fg<sup>-1</sup> as the current

density increases 20 times, from 1 to 20 Ag<sup>-1</sup> indicating that the NiCo<sub>2</sub>O<sub>4</sub>@NiMoO<sub>4</sub> electrode has a super high rate charge-discharge performance.



**Fig. 7.** (a) Specific capacitance as a function of discharge current density; (b) variation of specific capacitance with cycle numbers at a current density of 10 Ag<sup>-1</sup>.

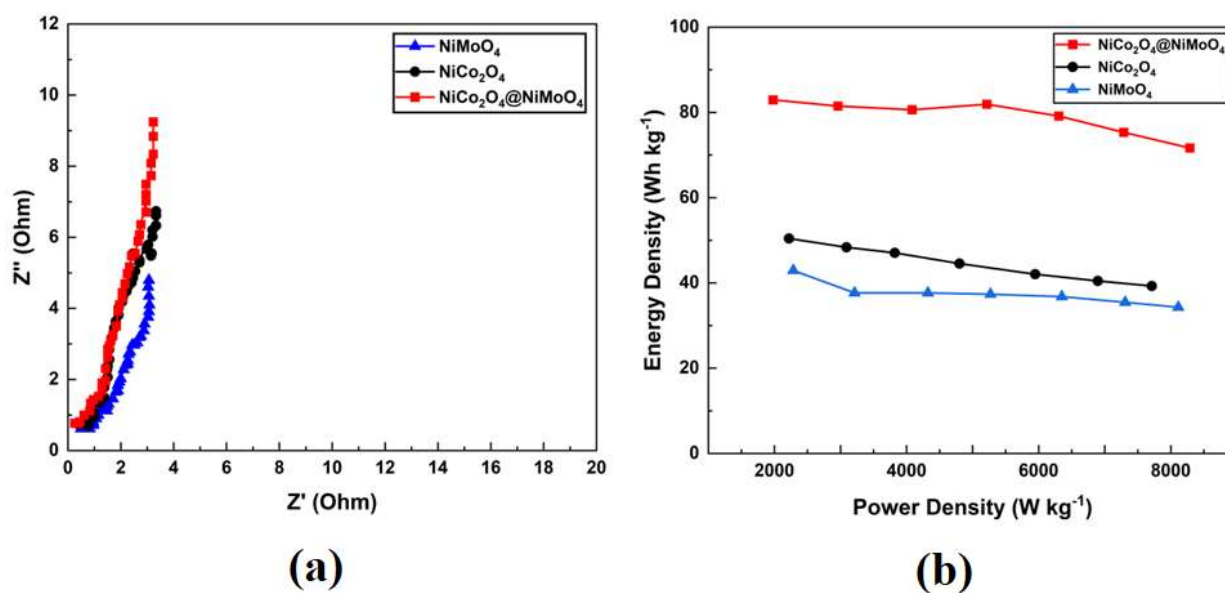
At 10 Ag<sup>-1</sup>, the cycle stabilities of the NiCo<sub>2</sub>O<sub>4</sub>, NiMoO<sub>4</sub> and NiCo<sub>2</sub>O<sub>4</sub>@NiMoO<sub>4</sub> electrodes were measured and the results are presented in Fig. 7(b). It is evident that after 1000 cycles at 10 Ag<sup>-1</sup>, the NiCo<sub>2</sub>O<sub>4</sub> and NiMoO<sub>4</sub> exhibit specific capacitances of 1064 Fg<sup>-1</sup> and 1492 Fg<sup>-1</sup> and capacitance retention of 95.6% and 98.2%, respectively. The NiCo<sub>2</sub>O<sub>4</sub>@NiMoO<sub>4</sub> hybrid electrode has a very high specific capacitance of 2356 Fg<sup>-1</sup> after 1000 cycles in addition to having a strong capacitance retention of 97.4%.

It is noteworthy that the specific capacitance of the NiCo<sub>2</sub>O<sub>4</sub>@NiMoO<sub>4</sub> electrode used in this research is also higher than that of other core-shell nano architected materials that have been previously described, as shown in Table 1.

**Table 1.** Comparison of core-shell nanoarchitecture materials

Reference	Nanomaterials	Method	Specific Capacitance Fg <sup>-1</sup> at 1 Ag <sup>-1</sup> )
[21]	NiCo <sub>2</sub> O <sub>4</sub> @NiCo <sub>2</sub> O <sub>4</sub>	Hydro	1917
[21]	NiCo <sub>2</sub> O <sub>4</sub> @NiO	Hydro	2105
[22]	NiCo <sub>2</sub> O <sub>4</sub> @graphene	Hydro	778
[23]	Co – NiO core-shell	Hydro	956
[24]	NiCo <sub>2</sub> O <sub>4</sub> @ NiMoO <sub>4</sub>	Hydro	2474
Proposed method	NiCo <sub>2</sub> O <sub>4</sub> @ NiMoO <sub>4</sub>	Microwave	<b>2724</b>

The hierarchical NiCo<sub>2</sub>O<sub>4</sub>@NiMoO<sub>4</sub> electrode and the EIS of NiCo<sub>2</sub>O<sub>4</sub>, NiMoO<sub>4</sub>, are displayed in Fig. 8(a). The semicircle is clearly visible in the inset and occurs frequently. All of the impedance spectra are comparable, consisting of a high-frequency semicircle followed by a low-frequency linear component. The two curves differ in two ways. First, the internal resistances ( $R_b$ ) in the high frequency intercept of the real axis were different. The  $R_b$  of NiCo<sub>2</sub>O<sub>4</sub>@NiMoO<sub>4</sub> electrode reduced when compared to NiMoO<sub>4</sub>, indicating that the addition of NiCo<sub>2</sub>O<sub>4</sub> enhanced the electrode's ability to conduct electrons. Second, the diffusive resistance (Warburg impedance) of the NiCo<sub>2</sub>O<sub>4</sub>@NiMoO<sub>4</sub> electrode was lower than that of NiMoO<sub>4</sub>, as shown by the straight line at low frequency. This finding suggests that the porous structure of the NiCo<sub>2</sub>O<sub>4</sub>@NiMoO<sub>4</sub> composite can lower the mass-transfer resistance and enhance the penetration of the electrolyte as well as ion diffusion in the host material. A minor pseudo charge transfer resistance ( $R_{ct}$ ), which corresponds to the minimal semicircle in the impedance plots, is also present in the NiCo<sub>2</sub>O<sub>4</sub>@NiMoO<sub>4</sub> electrode. The outstanding electrochemical capacitive characteristics of these binary metal oxide based composite materials are demonstrated by the low  $R_b$ ,  $R_{ct}$ , and Warburg impedance values.



**Fig. 8.** (a) AC impedance plots of three electrodes; (b) Ragone plot of the estimated specific energy and specific power at various charge–discharge rates.

We further compute the specific energy and power densities, which are the two crucial elements for the practical applications of electrochemical supercapacitors, in light of the high capacitance and great rate capability. Based on the following equations, one may get the specific energy density ( $E$ ) and power density ( $P$ ), respectively:

$$E = \frac{1}{2} C \Delta V^2$$

$$P = \frac{E}{\Delta t}$$

where  $C$  refers to the specific capacitance,  $E$  is the specific energy density,  $P$  represents the power density,  $\Delta V$  is the voltage range and  $\Delta t$  is the discharge time. In Fig. 8(b), the data are displayed as Ragone plots. The NiCo<sub>2</sub>O<sub>4</sub>@NiMoO<sub>4</sub> sample has the ability to produce high power outputs between 1485 and 8294 Wkg<sup>-1</sup>, with little loss of high energy density (between 83.5 to 79.2 Wh kg<sup>-1</sup>). The other two samples, however, show similar power densities with slightly lower but still striking energy densities. The current mesoporous NiCo<sub>2</sub>O<sub>4</sub>@NiMoO<sub>4</sub> hierarchical structures are very desirable as electrode materials for enhanced supercapacitors due to their remarkable ability to offer high specific power and energy densities.

According to the findings, the NiCo<sub>2</sub>O<sub>4</sub>@NiMoO<sub>4</sub> coreshell nanomaterial electrode has remarkable electrochemical performance as evidenced by its exceptionally high specific capacitance, low resistance, high cycle stability and capacitance retention, and good rate capability. All of these advantages are crucial for the real-world use in supercapacitors.

#### 4. Conclusion

In this study, heterostructures of pure NiCo<sub>2</sub>O<sub>4</sub> and NiCo<sub>2</sub>O<sub>4</sub>@NiMoO<sub>4</sub> were synthesized using a simple microwave irradiation approach, and their structural, morphological, and electrochemical analyses were conducted. The cubic crystal structure of the NiCo<sub>2</sub>O<sub>4</sub>@NiMoO<sub>4</sub> heterostructure was discovered using structural XRD measurements. By using HR-SEM and TEM to analyze the surface's morphology, the nanoplate-like structure of NiCo<sub>2</sub>O<sub>4</sub>@NiMoO<sub>4</sub> was observed. All prepared materials' elemental compositions and oxidation states underwent XPS analysis. The enhanced electro-chemical performance demonstrates that the inclusion of two metal oxides into a multifaceted core-shell hybrid nanostructure aligned with the electrically charged plates considerably increases the areal capacitance. The NiCo<sub>2</sub>O<sub>4</sub>@NiMoO<sub>4</sub> heterostructure demonstrated excellent supercapacitor performance with a high specific capacitance of 2724 F g<sup>-1</sup> at 1 A g<sup>-1</sup> and a high energy density of 83.5 Wh kg<sup>-1</sup> at a power density of 1485 W kg<sup>-1</sup>. This is according to electrochemical investigations on the synthesized materials in 1M KOH electrolyte. High recycling stability is also indicated by the device's high capacitance retention of 97.4 % after 1000 cycles of charge-discharge. As a result, the electrochemical research points to the NiCo<sub>2</sub>O<sub>4</sub>@NiMoO<sub>4</sub> heterostructure as a potential electrode material for supercapacitors' high-performance energy storage. The results show that any NiCo<sub>2</sub>O<sub>4</sub>@XMoO<sub>4</sub> core-shell electrode material has a high potential for use in electrochemical energy storage for supercapacitors employing microwave heating.

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