

Tuning electrochemical properties of Ni—Co MOF/MWCNTs composite via electrolyte optimization

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ABSTRACT

In pursuit of global energy demand the advancement of effective and eco-friendly electrode material is needed. In this study Ni—Co MOF/ MWCNTs composite was synthesized by solvothermal approach and was studied in various electrolytes (6 M KOH, 6 M LiCl, and 1 M Na₂SO₄) and their assessment was done via electrochemical approach using Cyclic Voltammetry (CV) for finding specific capacitance, Galvanostatic Charge Discharge (GCD) for determining energy density and power density, and Electrochemical Impedance Spectroscopy (EIS) studies to find solution and charge transfer resistance. GCD studies revealed the distinct behaviors based on ion properties, with KOH showing the highest ionic conductivity and capacitance retention (87.3 % at 4 Ag⁻¹). The specific capacitances (F g⁻¹), at 2 mVs⁻¹, were 1157.4 (KOH), 1022.3 (LiCl), and 736.5 (Na₂SO₄). The energy density and power density, at a current density of 0.5 A g⁻¹, were 205.90 Wh kg⁻¹ and 249.2 W kg⁻¹, respectively (in 6 M KOH). The capacitive retention of the composite Ni—Co MOF/MWCNT material is 87.3 % in 6 M KOH over 10,000 cycles. The study align with sustainable development goals (SDG7), focused on affordable, clean energy production and storage.

1. Introduction

Electronics devices are widely used for energy storage with high energy densities and long-lasting power densities [1]. Lithium-ion batteries (LIBs), due to their high energy density (E_d), have been vying with other battery technologies like lead-acid and nickel-cadmium batteries. However, LIBs can't meet the expectations of cutting-edge gadgets due to a lack of adequate power density and long-life cycle [2]. Compared to traditional batteries, SCs exhibit higher power density, longer lifespan, and safer chemistry, making them promising candidates for energy storage applications. In this scenario, LIBs are primarily employed in power backups, watches, wristbands, key bands, personal computers, and tablets as these devices require small, lightweight, environmentally cooperative energy storage components with high ED [3]. Due to their low energy density, supercapacitors still have limited practical applications [4]. Therefore, efforts must be made to enhance the supercapacitor's performance through the development of novel materials

including electrolytes. Depending on mechanism (faradic or non-faradic), capacitors are classified as Pseudo capacitors (PCs) and electrical double layer capacitors (EDLCs). PCs are composed of mainly conducting polymers and the first-row transition metal oxides, including Manganese (Mn), Nickel (Ni), Cobalt (Co), and Zinc (Zn) including their composites (binary and ternary) [3] with multiple oxidation states which strengthen the oxidation/ reduction potential of the material. Carbonaceous material such as graphene based, mesoporous carbon, carbon nanotubes and activated charcoal generally show non-faradic storage mechanism (as EDLCs). In this sequence although different class of materials including metal oxides [5,6], conducting polymers (PPy, PANI, PEDOT etc.) [7,8] and carbon based materials (Graphene, rGO, GO, g-C₃N₄ etc.) [9–12] have been employed for developing the electrode materials for energy storage application, but the researchers are still focusing for getting enhanced energy density using advanced materials. [13,14]

Metal-Organic Frameworks (MOFs) [15–17] are porous materials

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utilized for developing of electrodes owing to their varied characteristics such as sturdy framework [18], improved porosity [19], high specific surface area [20] with tunable pore dimensions. MOFs are used for gas filtration [21], light driven catalysis process [22], therapeutic delivery [23], sensing [24] and energy storage [4]. However, MOFs exhibit poor conductivity and hinder efficient ion transfer to the current collector, thus limiting their suitability for supercapacitor applications. Their hybrids with carbonaceous materials such as graphene, conductive polymers, and multi-walled carbon nanotubes (MWCNTs) can provide improved performance compared to pure MOFs. MWCNTs, which have excellent surface to volume ratios and length to diameter proportions are attractive electrode materials for supercapacitor applications. They have intriguing mechanical, electrical, structural and thermal behavior as well as clearly defined morphologies, and it is environmentally compatible. Due to the higher amount of transferable electrons, pseudo capacitors have a high specific capacitance and low resistance [25]. On other hand, carbonaceous material like mesoporous carbon, to provide sustained electrode materials for hybrid supercapacitors, composites composed of carbonaceous materials and transition metal MOFs have been developed. The development of novel materials for energy storage is the current interest of scientists. The sustainable composites of transition metals MOFs with carbonaceous material on their electrochemical performance have lately attracted attention, and it has been found that these properties depend on their morphological and structural characteristics. Therefore, we investigated how the inclusion of carbonaceous materials such as MWCNTs in Ni—Co MOF composite affects the electrochemical properties of hybrid supercapacitors. The main objective of research is to develop the energy storage materials using a suitable electrolyte. Due to the broader potential window, predominantly organic and ionic electrolytes are utilized with carbon-based materials in energy storage applications [26,27] which enhance the total energy density (E_d). This is attributed to the direct correlation between the E_d of the supercapacitor and the operating voltage. Although low conductivity, high cost and typical handling procedure are demerits of organic and ionic liquids versus aqueous electrolytes having low cost, sustainable, facile synthesis methods, excessive operating stability and correspondingly elevated ionic conductivity necessary for achieving reduced internal electrical resistance [28]. The aqueous electrolytes operate within a restricted voltage range versus organic electrolytes; the transport of ions is faster in case of former [29]. Therefore, initiatives are required to get the elevated potential windows for these electrolytes to expand the overall working potential window and E_d of the SCs. Limited number of studies are available in the area of concern. J. Zhu et al. studied the influence of different electrolytes containing cations (Li^+ , Na^+ , K^+ , and H^+) in a polypyrrole/rGO composite and its electrochemical properties [30]. They observed that the H^+ cations showed superior performance in 3 M HCl, due to their high ionic conductivity, faster electron transport rate, and shorter relaxation time period compared to the other electrolytes. L. Eliad et al. studied the evaluation of average size of ion in electrolyte solutions for porous carbonaceous electrode material [31].

In this work, we have investigated the influence of various aq. electrolytes (KOH, LiCl, and Na_2SO_4) on the electrochemical behavior of Ni—Co MOF/MWCNTs composite. The Ni—CoMOF/MWCNTs electrodes were studied for CV, GCD, EIS and cyclic stability measurements with all the three electrolytes to optimize the electrode and electrolyte combination.

2. Materials and methods

The chemicals used in materials preparation and processing were of analytical grade are N-Methyl pyrrolidone (NMP), Nickel nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 98.8 %), Cobalt nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$)(98.8 %), Trimesic acid (H_2BDC), Potassium hydroxide (KOH), and Ethanol purchased from Central Drug House (P) Ltd. – CDH, New Delhi. Nickel foils with thickness (0.5 mm, 99.98 % trace metal basis), ferrocene (98.0 %) and toluene (98.8 %) were purchased from

Sigma-Aldrich, United States. The all compounds were used untreated after being obtained from a commercial source.

2.1. Synthesis of multiwalled carbon nanotubes (MWCNTs)

The chemical vapour deposition (CVD) method was used to synthesize Multi-walled carbon nanotubes (MWCNTs) (shown in Fig. 1). A mixture of ferrocene and toluene (1:3) was introduced into a quartz tube at a controlled flow rate (6 mL/h) using a syringe pump. The quartz tube consisted of a two-stage furnace, where the reaction zone was maintained at 750 °C under ambient conditions with argon environment (flow rate of 2 L/min) to maintain an inert atmosphere. Upon completion of the synthesis, the resulting MWCNTs were collected by scraping the inner surface of the quartz tube [32].

2.2. Synthesis of metal organic framework (Ni—Co MOF)

Metal ions from the respective hexahydrate nitrate salts of Ni and Co were used to synthesize Ni/Co-MOF taking trimesic acid (TMA) as an organic linker. Simple hydrothermal method was employed to synthesize MOF (Ni—Co MOF) following the procedure in literature. In 40 mL of *N,N*-dimethylformamide DMF, 1.5 mmol of each of the hexahydrate nitrates of nickel and cobalt were dissolved, then the solution mixture was shaken at room temperature. TMA was reacted with Ni^{2+} and Co^{2+} ions in a Ni:Co:TMA mole ratio of 1.5:1.5:2 to synthesize Ni—Co MOF. The resulting vivid purple solution was stirred for 30 min before being decanted into a 100 mL stainless Teflon lined steel autoclave and subjected to dry at 160 °C for 18 h. Once it has cooled to room temperature, the precipitates are repeatedly washed by centrifugation with ethanol and DMF. The final product was configured for drying (24 h, 80 °C) in a high vacuum oven. Ni/Co MOFs were dried and ground into a light purple powder as a sample (shown in Fig. 1). Based on the metal ions that were present in the solution, Ni/Co-MOFs with a light purple tint were produced [3].

2.3. Ni—Co MOFs composites with MWCNTs

The solvothermal method was used to synthesize the Ni—Co MOF/MWCNTs composite material. Firstly, MWCNTs particles dispersed in acidic mixture (98 % H_2SO_4 —68 % HNO_3 , 3:1 ratio) by ultrasonication and further refluxed (At 110 °C, 5 h). The desired precipitates were thoroughly washed with distilled water to attain neutrality and dried at 70 °C in vacuum oven and carboxylated MWCNTs were obtained. Then, in 5 mL of DMF, 0.5 mg of carboxylated MWCNT was dispersed and after that 0.125 mmol of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and an equimolar amount of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were added and stirred for 1 h to form suspension A. In a separate beaker 0.167 mmol of Trimesic acid in 17 mL DMF-EtOH was added in volume ratio of 15/2 to form solution B. This solution is gradually added in suspension A and again stirred for 1 h. It was then put into vacuum oven (160 °C, 12 h). Precipitations were cleaned multiple times with distilled water and ethanol and at last black coloured Ni—Co MOF/MWCNTs composite is obtained (shown in Fig. 1) [33].

2.4. Characterization of material

The materials (reported in Sections 2.2 and 2.3) were characterized using X-Ray Diffraction, Field Emission Scanning Electron Microscopy FESEM (EDS), Raman spectroscopy and Brunauer-Emmett-Teller analysis. X-ray diffractometer (XRD, Rigaku Smart Lab 3 kW) equipped with a $\text{Cu-K}\alpha$ radiation source ($\lambda = 1.540 \text{ \AA}$) was used to study the crystal features of the synthesized samples. The instrument operated at a constant filament intensity of 25 mA and a power of 45 kV. Data collection was performed over a 2θ range of 5° to 90°, employing a slow scan rate of 2°/min with a step size of 0.02°. The surface morphology and topography of the prepared samples were examined using FESEM (FE-SEM, Zeiss Gemini SEM 500 Thermal field emission type). SEM Micrographs

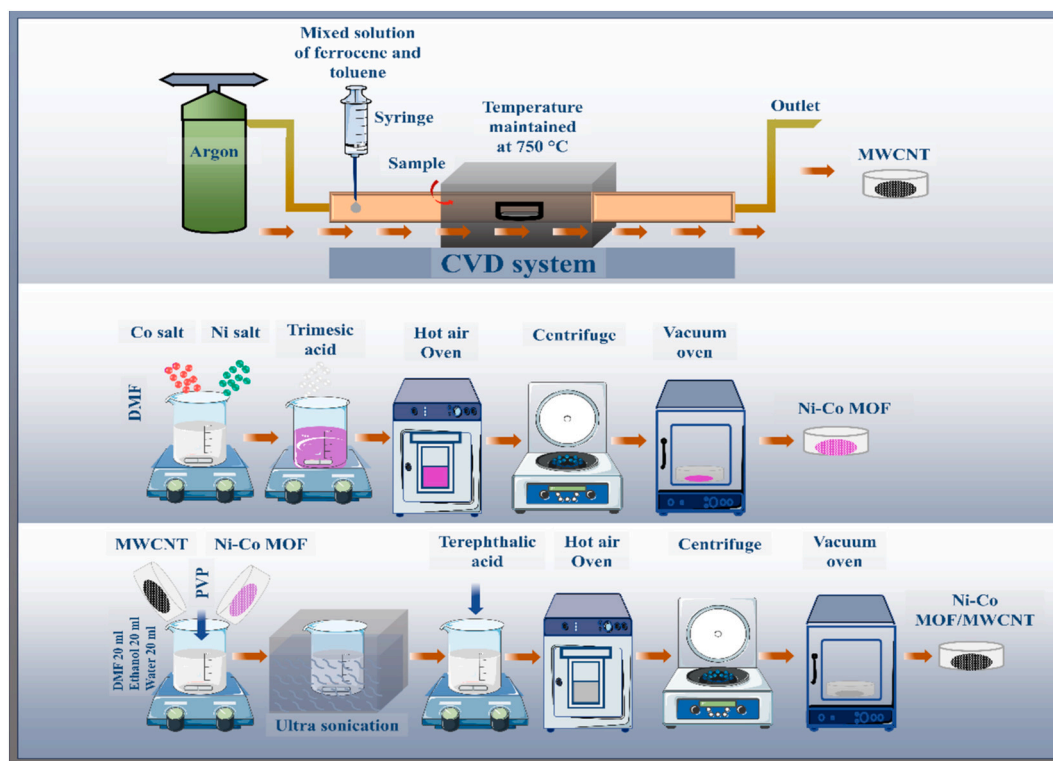


Fig. 1. Synthesis of MWCNTs, Ni—Co MOF and Ni-Co MOF/MWCNTs.

were taken at several magnifications with an accelerating voltage of 10 kV. Energy dispersive X-ray spectroscopy (SEM-EDS) was employed to determine the elemental composition of the materials together with weight% and atomic%. For chemical analysis and confirming the successful synthesis of MWCNTs, synthesized samples were studied using Raman spectrophotometer (WITec Alpha300 model). Nitrogen (N_2) adsorption-desorption analysis was performed using a Quantachrome Autosorb iQ Station 2 to evaluate the specific surface area and average pore size of the synthesized samples, based on the Brunauer-Emmett-Teller (BET) model. XPS was carried out to study surface chemistry and chemical states of metal ions using PHI 5000 VersaProbe III setup.

3. Result and discussion

3.1. X-ray diffraction

The XRD analysis of MWCNTs, Ni—Co MOF, and Ni—Co MOF/MWCNTs composites was performed using a SmartLab 3 kW (Rigaku) system, and the corresponding diffraction patterns are shown in Fig. 2 (a). Using JCPDS database the observed results were compared for materials. XRD results for MWCNTs (Fig. 2(a)) indicate values at 25.9 (002) and 43.1(100) of 2 θ , as illustrated in Fig. 2 (a)(JCPDS 41-1487) [34]. The primary characteristics of the X-ray diffraction pattern of CNTs are comparable to those of graphite because of the inherent properties of CNTs. Fig. 2(b) represents the XRD pattern of Ni—Co MOFs Peak (represented by purple line) corresponding to 2 θ values at 12.4°, 15.4°, 17.6°, 18.8°, 23.7°, 29.1°, 31.5°, 40.9° and 44.6° exhibited in this work which shows the successful formation of Ni—Co MOF crystals by trimesic ligands. Also, in Fig. 2(b) the diffraction patterns of Ni—Co MOF/MWCNTs composite (represented by magenta line) is shown which demonstrates that the presence of MWCNTs particles do not disturbed the Ni—Co MOFs crystal structure. The pattern's strong peaks attest to the composite's crystallinity. Furthermore, Ni—Co MOF/MWCNTs composite have two weak peaks corresponding at 25.9 (002) and 43.1(100) due to the presence of MWCNTs nanoparticles in it [32].

3.2. Surface chemistry

The functional group analysis of all the synthesized samples (MWCNTs, Ni—Co MOF and Ni—Co MOF/MWCNTs composite) are as shown in Fig. 2(c) and (d). An absorption peak in MWCNT at 1632 cm^{-1} is related to C=C stretching vibration of graphitic structure in network. O—H symmetric stretching vibration peak is at 3420 cm^{-1} . Peaks at 2930 cm^{-1} and 2848 cm^{-1} are due to $-CH_2$ and $-CH_3$ stretching vibrations. C=O stretching vibrations peak appeared at 1738 cm^{-1} . Shoulder at 1444 cm^{-1} arises due to C=C stretching of aromatic structure. Peaks from C-O-C arise at 1396 cm^{-1} and 1094 cm^{-1} in MWCNTs, 775 cm^{-1} and 678 cm^{-1} is characteristic peaks of benzene ring [35]. Absorption Peaks at 3468 cm^{-1} and 2863 cm^{-1} arises in Ni—Co MOFs due to $-OH$ hydroxyl group and $-CH$ stretching vibrations, respectively [3]. Peaks present at 1105 cm^{-1} and 761 cm^{-1} are attributed to aromatic ring and plane deformation, respectively [33]. A shoulder appears at 1370 cm^{-1} and 1590 cm^{-1} , corresponding to the symmetric and asymmetric stretching modes of carboxyl functional groups, respectively. Co—O stretching vibrations cause the peak at 679.9 cm^{-1} to appear [33]. Presence of hydroxyl group in the Ni—Co MOFs/MWCNTs composite is responsible for the absorption peak at 3477 cm^{-1} [33]. The peak at 1629 cm^{-1} is due to coordinated ($-COO$) group because of asymmetric elongation. The symmetric stretching of the carboxyl group causes an absorption band to form at 1367 cm^{-1} . Peaks observed at 1104 and 758 cm^{-1} are caused by the vibration of the aromatic ring's $-CH$ ring and plane. The shoulder at 626 cm^{-1} is because of the expansion vibrations of para-aromatic C—H bond and the bending motion of hydroxyl ($-OH$) groups [3].

3.3. Morphological studies (SEM)

The surface morphological analysis of synthesized materials was performed via FESEM analysis (7610 F Plus/ JEOL). The diameter of MWCNTs were found to be 5.7 nm to 96.9 nm and length to few microns as shown in Fig. 3 (a, b). It has tube like structures grown perfectly

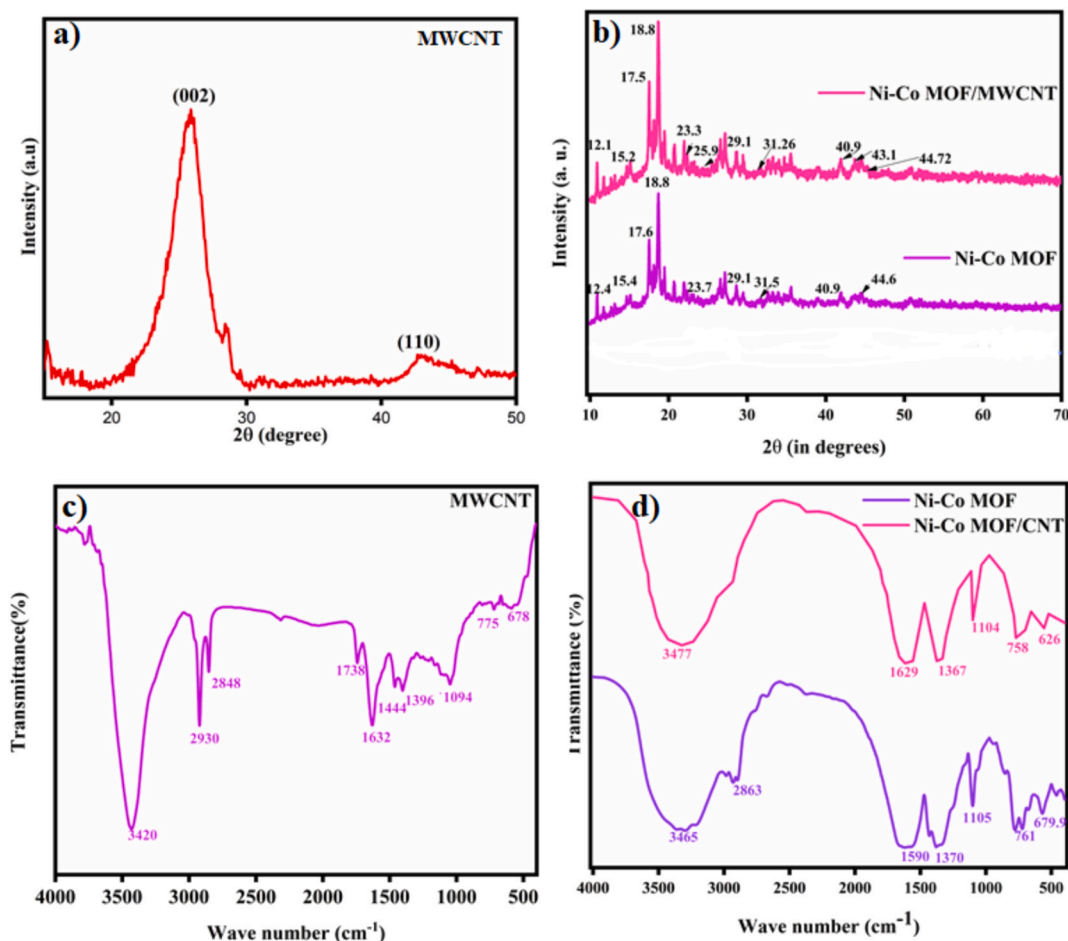


Fig. 2. p-XRD spectra of (a) MWCNTs (b) NiCo-MOF and NiCo-MOF/MWCNTs; FTIR spectra of (c) MWCNTs, (d) NiCo-MOF and NiCo-MOF/MWCNTs.

cylindrical structure of seamless graphite. The morphological images of NiCo-MOF and NiCo-MOF/MWCNT nanocomposites are shown in Fig. 3 (c, d, e and f). It is evident that the porous nano-composites (Ni—Co MOFs) display a structure of nanosheets that range in size from 52.9 nm to 176 nm. It was noticed that the internal framework of nanorods is more uniformly distributed compared to that in Ni-MOF clusters. The strong firm is there between NiCo-MOF nanosheets and MWCNTs surface in parallel due to metal-ligand coordination between metal ions and MWCNTs carboxyl groups, along with hydrogen bonding between carboxyl groups of both components. To analyse the elemental composition, the synthesized materials were examined using Energy Dispersive X-ray Spectroscopy (EDS). The EDS spectra of the material (Fig. 3g) confirm the existence of anticipated elements: carbon (from the organic linker and MWCNTs), oxygen (from the organic linker), cobalt and nickel (from metal precursors). The corresponding weigh percentages are 44.4 %, 40.4 %, 6.5 % and 8.5 % while the atomic percentages are 57.0 %, 39.1 %, 1.7 % and 2.2 % respectively.

3.4. Raman spectroscopy

Raman spectroscopy was employed to investigate the vibrational modes and molecular-level interactions in the synthesized samples. In the Raman spectrum of pure MWCNTs, two prominent bands are observed: the D band around 1350 cm^{-1} , which is associated with defects, structural imperfections, and disorder in the sp^2 carbon network, and the G band near 1580 cm^{-1} , corresponding to the graphitic (sp^2 -hybridized) carbon framework, reflecting the degree of graphitization. In the NiCo-MOF/MWCNTs composite, additional Raman features appear. The peaks around $800\text{--}900 \text{ cm}^{-1}$ are attributed to metal–oxygen

(M–O) stretching vibrations (M = Ni or Co), indicating the successful coordination between the metal centers and oxygen atoms of the organic ligand. A noticeable peak near 1000 cm^{-1} corresponds to the symmetric ring breathing vibration of the BTC (benzene-1,3,5-tricarboxylic acid) linker, suggesting the integrity and preservation of the aromatic framework in the MOF structure. The D band ($\sim 1350 \text{ cm}^{-1}$) is again visible in the composite, indicating that structural defects or edge states in MWCNTs persist even after composite formation. Interestingly, a sharp peak around 1400 cm^{-1} is also observed, which is because of C=C bond stretching vibrations within the benzene ring of the BTC linker, or possibly due to modified carboxylate symmetric stretching influenced by the interaction between BTC and metal ions. This may reflect strong electronic interactions or π – π stacking between the MOF and MWCNTs components. Finally, the G band ($\sim 1580 \text{ cm}^{-1}$) is retained in the composite, further confirming the presence of ordered graphitic domains of MWCNTs. The overall Raman profile suggests successful integration of MWCNTs within the NiCo-MOF matrix, with clear indications of molecular interaction, coordination bonding, and structural integrity of both components. [36–38] (shown in Fig. 4).

3.5. X-ray photoelectron spectroscopy (XPS)

XPS was carried out to analyse properties such as elemental composition, chemical environments and chemical states of the metal ions embedded the composite material. Since our composite consists of Ni—Co MOF integrated with MWCNTs, peaks corresponding to carbon, oxygen, nickel, and cobalt are expected. Accordingly, all corresponding peaks were confirmed using X-ray photoelectron spectroscopy (XPS), as shown in Fig. 5(a). A peak at 284.5 eV in the high resolution spectra of C

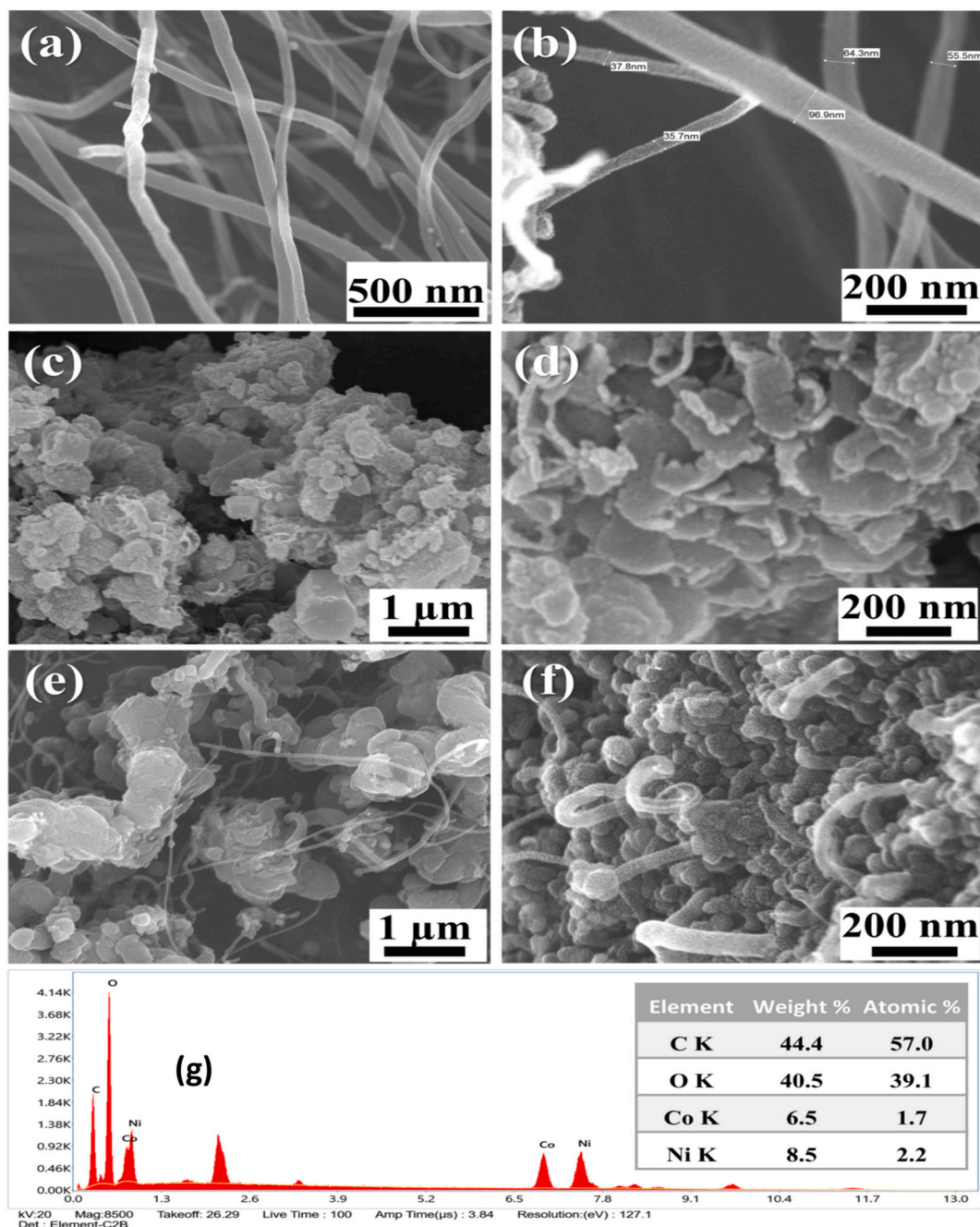


Fig. 3. Morphological analysis of (a, b) MWCNTs, (c,d) Ni-Co-MOFs, (e, f) NiCo-MOFs/MWCNTs composite and (g) Elemental mapping of Ni-Co MOF/MWCNTs composite.

1 s was noticed due to the presence of C=C while peaks at 288.6 eV and 285.09 eV were due to the presence of C=O in organic ligand and C—O bond (Fig. 5 (b)). The peak at 288.6 eV was found to be shifted as compared to previous studies which may be due to the interaction between MWCNT and NiCo-MOF. Peaks at 530.1 eV, 531.7 eV and 530 eV in high resolution spectra of O 1 s were identified due to the presence of Ni—O, C—O and O—C=O bonds (Fig. 5 (c)). High resolution spectra of Ni 2p and Co 2p spectra were found to split into various peaks due to the presence of multiple oxidation states of Nickel and cobalt. Peaks at 855.87 eV, 861.42 eV, 872.67 eV and 874.78 eV were present due to the multiple oxidation states of Nickel (Ni^{2+} and Ni^{3+}) (Fig. 5 (d)). In high resolution spectra of Co several peaks were found again due to the presence of multiple oxidation states of Cobalt (Co^{2+} and Co^{3+}) (Fig. 5 (e)). [39,40]

3.6. Specific surface area (SSA) and pore size distribution (BET)

Surface characteristics of material such as SSA, pore diameter, and pore size distribution were determined using Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH methods). N_2 adsorption desorption isotherms of all the synthesized materials were performed using Quantachrome Instruments version 5.21. Fig. 6(a-c) represents the BET sorption isotherms for MWCNTs, NiCo-MOF and NiCo-MOF/MWCNT respectively. Table.1 represents SSA, specific pore volume (PV) and average pore diameter (PD). The higher SSA ($187.24 \text{ m}^2 \text{ g}^{-1}$) of NiCo-MOF/MWCNTs shows that MWCNTs prevent the agglomeration of NiCo-MOF leading to enhancement of electrochemical performance. BJH model demonstrates typical type IV [41] isotherms consisting a hysteresis loop in a relative pressure range (0.2–0.9), 1st loop indicates

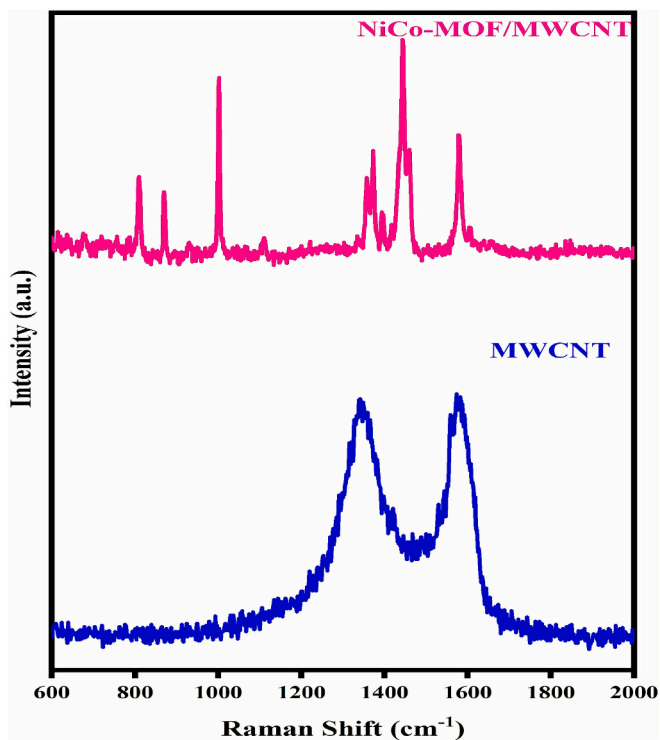


Fig. 4. Raman spectra of MWCNTs and NiCo-MOF/MWCNTs composite.

the adsorption and 2nd loop indicates the desorption. As shown in the Table, the mean pore diameter ranges from 2 to 50 nm, indicating the mesoporous structure of the material [41].

4. Preparation of electrodes and electrochemical measurements

Active material, carbon black and PVDF in the ratio of (8:1:1) were taken to fabricate the electrodes. Then, for making homogeneous slurry *N*-methyl pyrrolidone (NMP) was used as a solvent after that it is deposited over a nickel foil (1×1) cm using drop casting method. For 24 h, the prepared electrodes were subjected to dry at 80°C temperature in vacuum hot air oven (shown in Fig. 7). A three-electrode setup was used for electrochemical studies which was composed of a working electrode, reference electrode (Ag/AgCl) which provide a stable potential window while a Platinum (Pt) wire electrode was employed to complete the electrical circuit and facilitate the transport of electrons during electrochemical processes. Electrochemical investigations of composite material Ni/Co-MOF-MWCNTs were carried out using CV, GCD and EIS using 6 M KOH, 6 M LiCl and 1 M Na_2SO_4 as electrolytes.

4.1. Cyclic voltammetry

CV studies of composite (NiCo-MOF/MWCNTs) were performed using 6 M KOH, 6 M LiCl and 1 M Na_2SO_4 as electrolytes at 2 mVs^{-1} scan rate. The capacitance for the working electrodes in case of different electrolytes using I-V plot were calculated using the formula

$$C = \frac{\int Idv}{m \times s \times \Delta V} \quad (1)$$

Here, C (specific capacitance, F g^{-1}), I (electrode current, A), s (scan rate, mV s^{-1}), ΔV (potential window, V), and m (mass deposited on the electrode, mg) represent the respective parameters. The specific capacitance of Ni/Co-MOF-MWCNTs composite were 1157.4 F g^{-1} , 1022.3 F g^{-1} , and 736.5 F g^{-1} in 6 M KOH, 6 M LiCl, and 1 M Na_2SO_4 aqueous electrolytes, respectively, at a scan rate of 2 mV s^{-1} . These variations in capacitance can be attributed to the differing physicochemical

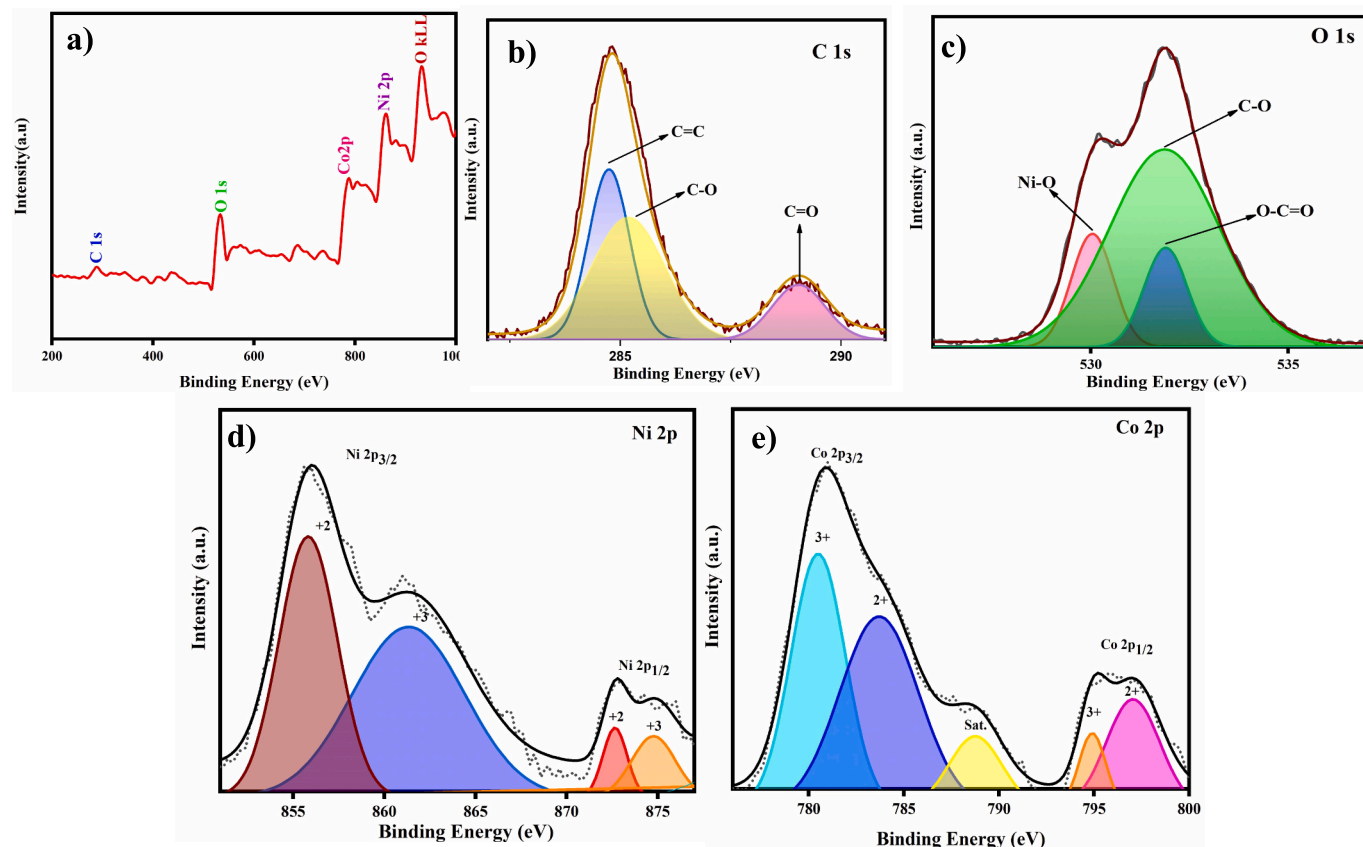


Fig. 5. a) Survey spectra of NiCo-MOF/MWCNTs composite, b-e) High resolution XPS spectra of C 1s, O 1s, Ni 2p and Co 2p

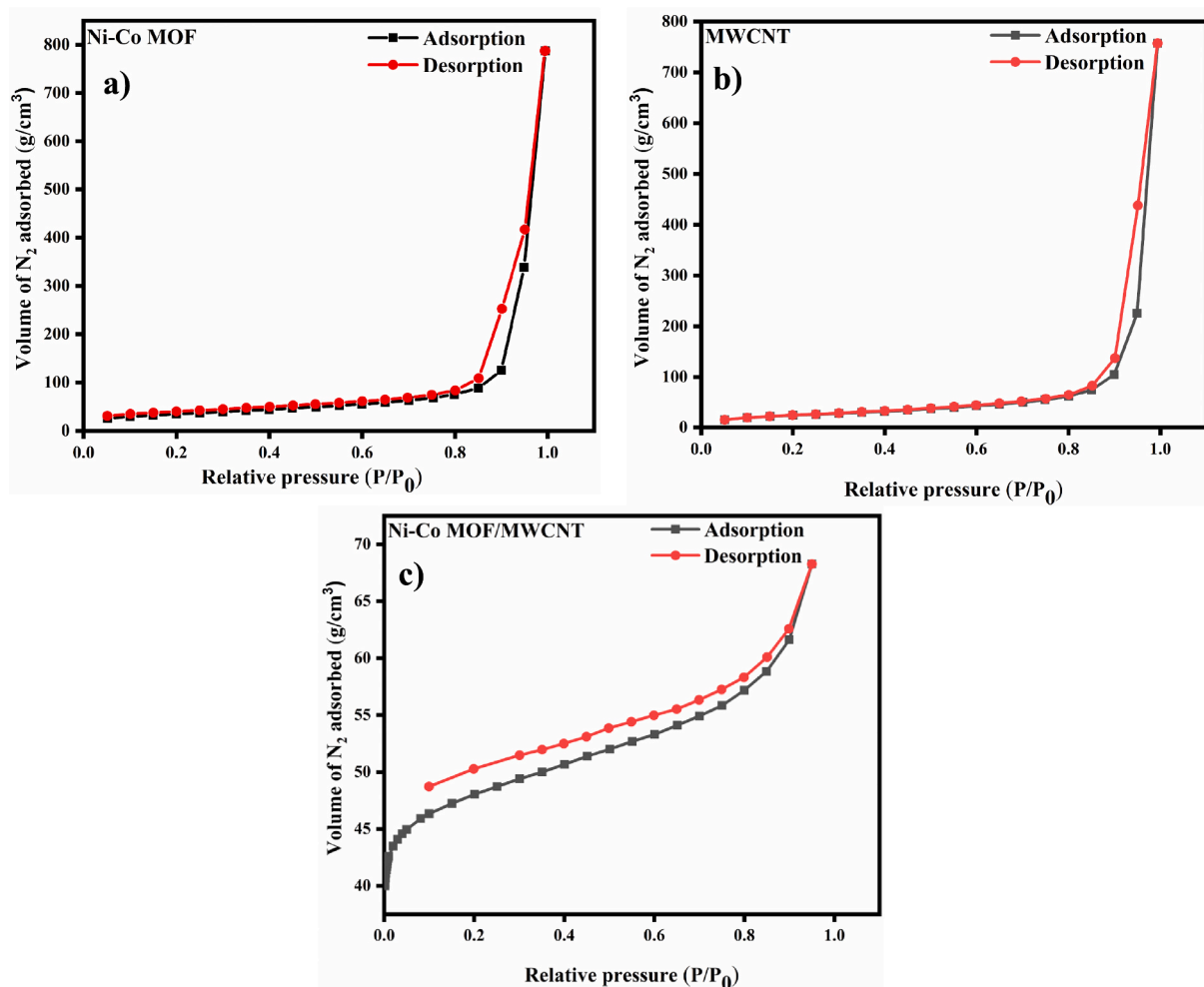


Fig. 6. a-c) N_2 sorption isotherm of Ni-Co-MOF, MWCNTs and NiCo-MOF/MWCNTs composite.

Table 1

Specific surface area (SSA), pore volume and mean pore diameter of MWsNTs, Ni—Co MOFs and Ni—Co MOF/MWCNTs.

Sample	SSA ($m^2 g^{-1}$)	Pore Volume ($cm^3 g^{-1}$)	Average pore diameter (nm)
MWCNTs	89.741	1.185	31.12
Ni-Co MOF	123.09	1.22	17.54
Ni-Co MOF/MWCNTs	187.24	0.032	3.815

properties of the electrolytes, which significantly influence the cyclic voltammetry (CV) behavior. As a result, the CV curves at 2 mV s^{-1} exhibit distinct profiles, as illustrated in Fig. 8(a). The key physical factors affecting electrochemical performance include ionic radius, hydration sphere radius, molar conductivity, and ionic mobility, with their respective values presented in Table 2. Among alkali metal cations, the hydration sphere radius follows the order as $Li^+ > Na^+ > K^+$, owing to their high solubility in water. As listed in Table 2, Li^+ has a hydration sphere radius of $3.82 \text{ \AA}$, whereas Na^+ and K^+ exhibit $3.58 \text{ \AA}$ and $3.31 \text{ \AA}$, respectively. However, in bulk electrolytes, the hydration shell is dynamic, meaning the number of water molecules surrounding each cation is not rigidly fixed. Consequently, ionic mobility and conductivity work as important factor in governing the electrochemical response of the electrodes examined in this study. Moreover, the presence of the SO_4^{2-} anion, being relatively larger in size, impedes the movement of Na^+ in Na_2SO_4 electrolyte, thereby negatively affecting supercapacitive performance. This suggests that although Li^+ has lower molar conductivity

in comparison to Na^+ , the capacitive behavior in Na_2SO_4 may still be inferior due to hindered ion transport. Following the acquisition of I-V plots, the data were analyzed, and Eq. (1) was employed to calculate C_s from CV measurements [45]. During the calculations, the mass (mg) was converted to grams and the scan rate (mV s^{-1}) to V s^{-1} ensuring that the specific capacitance is expressed in Fg^{-1} . Furthermore, as the scan rates increasing, the KOH exhibits a stable capacitance as compared to other two electrolytes; having specific capacitance ($1157.4, 972.3, 740.7, 451.4, 219.8$ and 134.2 Fg^{-1}) at scan rates ($2, 5, 10, 20, 50$ and 100) mVs^{-1} respectively as shown in Fig. 9 (a). The oxygen containing functional groups and presence of surface carbonyl that may lead to redox reactions with the KOH electrolyte and correspondingly increase the stability of the electrode material. [44].

4.2. Galvanostatic charge discharge

The charge-discharge curves of the composite Ni—Co MOF/MWCNT in the three different electrolytes (KOH, Na_2SO_4 , and LiCl aqueous electrolytes) is shown in Fig. 8(b). The observed non-symmetric charge/discharge profiles suggest the pseudocapacitive behavior of the composite, contributing to the overall specific capacitance. At 0.5 A/g current density, the C_s values are 1482.5 Fg^{-1} , 1270.2 Fg^{-1} , and 1010.5 Fg^{-1} in KOH, Na_2SO_4 , and LiCl aqueous electrolytes, respectively. The charge/discharge curves in 6 M KOH exhibit nearly ideal isosceles triangular shapes, signifying the exceptional electrochemical stability of the composite in this medium. The suitability of KOH as an electrolyte can be attributed to its high ionic conductivity, which enhances charge

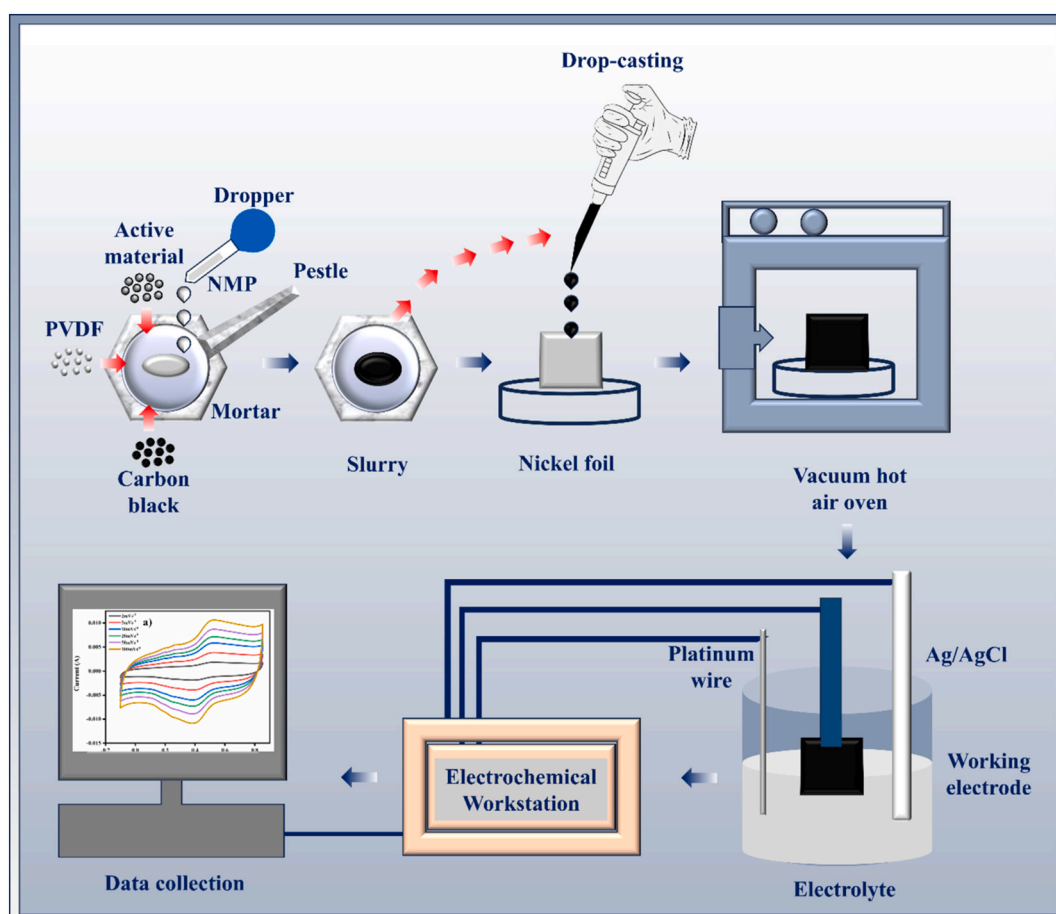


Fig. 7. Electrode preparation using NiCo-MOF/MWCNTs composite.

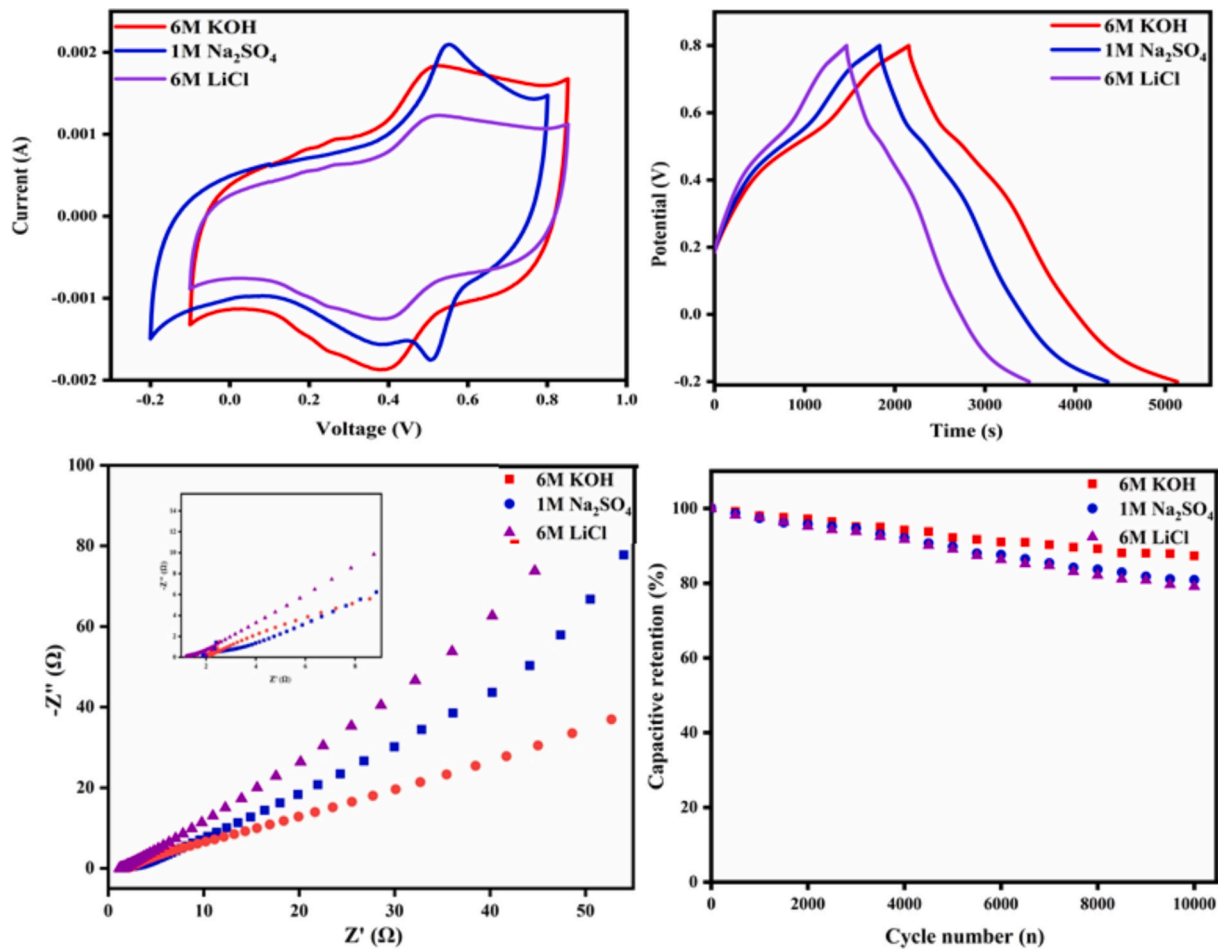


Fig. 8. a) CV plots for NiCo-MOF/MWCNTs composite with electrolytes (6 M KOH, 1 M Na₂SO₄ and 6 M LiCl) at 2 mV s⁻¹ scan rate b) GCD plots for NiCo-MOF/MWCNTs composite with different electrolyte c) EIS plots for NiCo-MOF/MWCNTs composite with different electrolyte and d) Cyclic stability curve for NiCo-MOF/MWCNTs composite with different electrolyte.

Table 2

Crystal radius, radiation of hydration sphere, molar conductivity and ionic mobility of alkali metal ions in water (At 25 °C) [42–44].

Alkali ion	Crystal radius (Å)	Radius of hydration sphere (Å)	Molar conductivity (cm ² Ω ⁻¹ mol ⁻¹)	Ionic mobility (μ10 ⁻⁵ cm ² s ⁻¹ v ⁻¹)
Li ⁺	0.60	3.82	38.6	–
Na ⁺	0.95	3.58	50.1	5.2
K ⁺	1.33	3.31	73.5	7.6
Cl ⁻	1.70	3.14	76.4	–
SO ₄ ²⁻	–	3.79	79.8	8.3
OH ⁻	–	3.00	198.0	20.6

transport, accelerates charge-discharge processes, and improves ion diffusion. Additionally, it exhibits excellent electrochemical stability and ionic conductivity within a potential window. The remarkable electrochemical behavior and stability of the composite in KOH highlight its strong potential for supercapacitor applications. The C_s from Galvanostatic charge discharge curves, along with the E_d and P_d of the electrode material, are determined using Eqs. (2), (3), and (4), respectively [46].

$$\text{Specific Capacitance } (C_s), C = \frac{I \Delta t}{m \Delta V} \quad (2)$$

$$\text{Energy density } (E_d), E = \frac{C \Delta V^2}{7.2} \quad (3)$$

$$\text{Power density } (P_d), P = \frac{3600 E}{\Delta t} \quad (4)$$

where, Δt (seconds) denotes the discharge duration, m (mg) corresponds to the mass of the active material on the electrode, ΔV (volts) signifies the voltage window, E_d have unit W h Kg⁻¹, and P_d have unit W Kg⁻¹. The E_d and P_d of the composite were determined to be 205.90 W h Kg⁻¹ and 249.2 W Kg⁻¹, respectively, at a current density of 0.5 A g⁻¹, as calculated using Eqs. (3) and (4). GCD curves of NiCo-MOF/MWCNTs composite corresponding to the different current densities in 6 M KOH are shown in Fig. 9 (b) and the specific capacitance were (1482.51221, 730 and 576) Fg⁻¹ at current densities (0.5, 1, 2 and 4) Ag⁻¹ respectively. Higher current density offers unwanted faradic reactions and erodes electrode material which conversely reduces specific capacitance. The capacitive retention of the composite Ni—Co MOF/

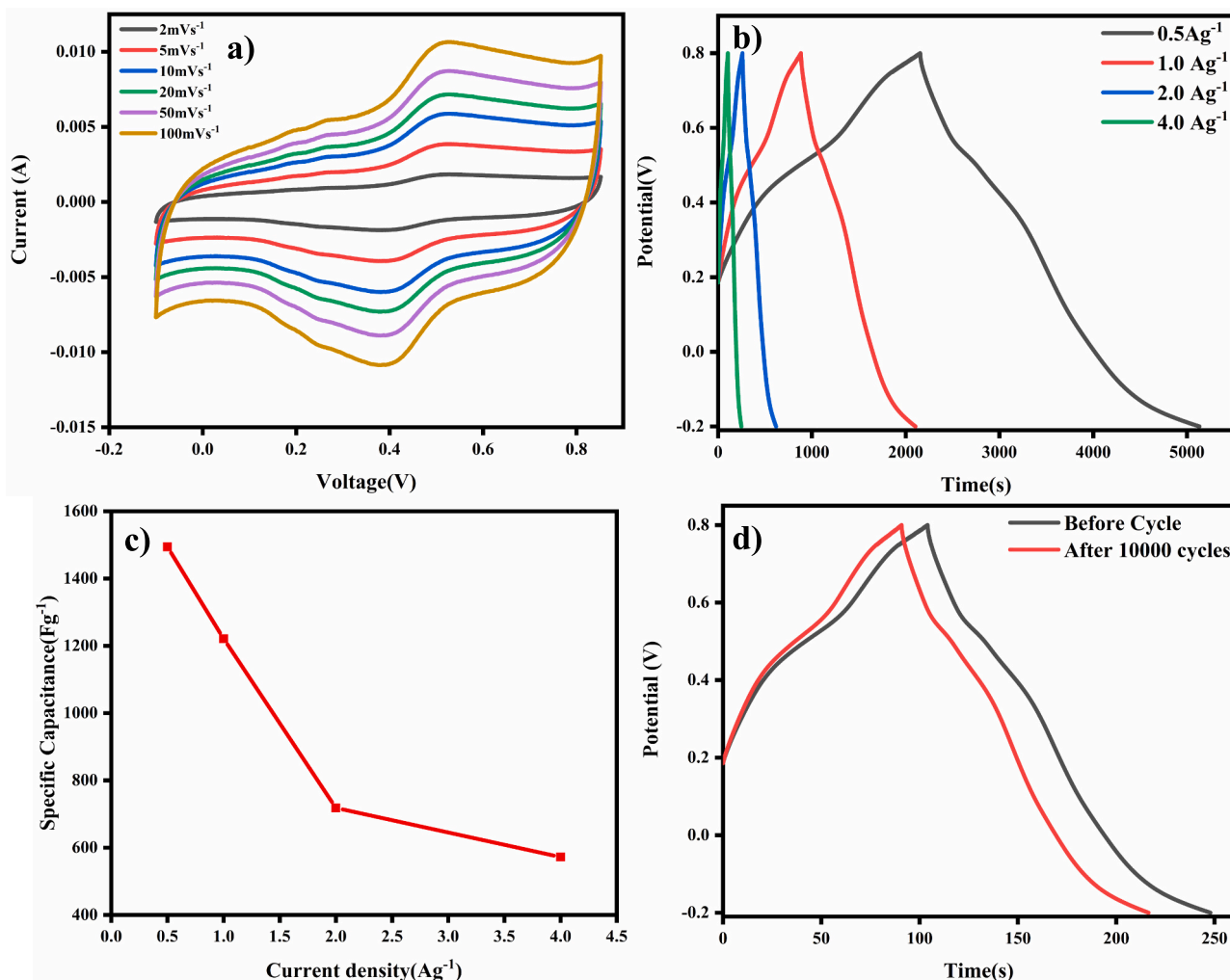


Fig. 9. a) CV curves for NiCo-MOF/MWCNT composite at scan rates, b) GCD curves for NiCo-MOF/MWCNT composite at different current densities, c) Plot for specific capacitance vs current density for composite and d) Cyclic stability curve for composite before and after 10,000 cycles.

MWCNTs material is 87.3 % in 6 M KOH while in 1 M Na₂SO₄ and 6 M LiCl retention is 82.4 % and 79.7 % over 10,000 cycles (shown in Fig. 9 (d)). Coulombic efficiency (η) is an important parameter for evaluating the effectiveness and reversibility of the charge storage mechanism in electrochemical systems. A high Coulombic efficiency indicates that ions are readily and reversibly intercalated and deintercalated during galvanostatic charge-discharge cycles. Therefore, it provides insight into the stability and durability of the electrochemical process over cycling. The Coulombic efficiency (%) of the prepared samples was determined using the Eq. (5) [47].

$$\eta = \frac{t_1}{t_2} \times 100 \quad (5)$$

Here, t_1 and t_2 denote the discharge and charge durations, respectively. In this study, the Coulombic efficiency of the composite was determined to be high, indicating its excellent charge retention capability. Such a high Coulombic efficiency suggests exceptional electrochemical reversibility and minimal energy loss during cycling. The value exceeding 100 % can be attributed to additional faradaic reactions, surface redox processes, and pseudocapacitive contributions, which enhance charge storage beyond the expected capacitive limits. The synergy between NiCo-MOF/MWCNTs and the 6 M KOH electrolyte

plays a crucial role in this phenomenon, as the strong alkaline environment facilitates rapid ion diffusion and promotes reversible redox transitions of Ni and Co species. This enhances charge storage efficiency and leads to an extended discharge time compared to the charge time, resulting in a Coulombic efficiency greater than 100 %. The outstanding performance of the composite in 6 M KOH further underscores its potential for high-performance supercapacitor applications, ensuring efficient ion transport and enhanced cycling stability.

4.3. Electrochemical impedance spectroscopy

The Nyquist plots of Ni—Co MOF/MWCNTs composite in different electrolytes, as obtained from EIS measurements are shown in Fig. 8(c). All three plots exhibit a nearly identical capacitive profile, characterized by a vertical trend in the low-frequency region and minimal diffusion resistance. This variation primarily reflects differences in the solution resistance (R_s) values of the composite in the three different electrolytes. The R_s value for KOH is recorded as 1.93 Ω , which is significantly lower than the values observed for LiCl (2.13 Ω) and Na₂SO₄ (2.7 Ω). Similarly, the charge transfer resistance (R_{ct}) follows the same increasing trend as R_s . The EIS analysis further confirms that K⁺ ions possess the highest molar conductivity in comparison to Li⁺ and Na⁺ ions, leading to the

lowest R_s and R_{ct} values, thereby enhancing ionic transport and overall electrochemical performance.

Declaration of competing interest

Material	Synthesis method	Substrate	Electrolyte	Capacitance retention	Energy density (Wh kg ⁻¹)/power density (W kg ⁻¹)	Reference
MnNi-MOF@CNT	Solvothermal method	Ni foam	1 M LiOH	74.92 % after 1000 cycles	33.2/1198	[48]
MWCNT@Ni(BTC)	Solvothermal method	Ni foam	2 M KOH	81.6 % after 5000 cycles	–	[49]
ZIF-67/Mn /MWCNT/ LDH	Solvothermal method	Ni foam	2 M KOH	92 % after 1000 cycles	70/244	[50]
NiCo- MOF/MWCNT	Solvothermal method	Ni foam	2 M KOH	98 % after 3000 cycles	20.2/250	[33]
Ni-MOF/MWCNT	Solvothermal method	Graphite paper	6 M KOH	82 % after 1000 cycles	31.66/249	[51]
rGO/MWCNT	Chemical oxidation	Ni foam	2 M KOH	85 % after 10,000 cycles	29.4/439	[52]
Cu-MOF/MWCNT	Hydrothermal method	Ni foam	1 M KOH	98.3 % after 15,000 cycles	47/920	[53]
NiCo- MOF/MWCNT	Solvothermal method	Ni foam	6 M KOH	87.3 % after 10,000 cycles	205.90/249.2	This work

5. Conclusion

In this work solvothermal approach was used to synthesize Ni—Co MOF/MWCNTs composite followed by its application as an electrode in different electrolytes 6 M KOH, 1 M Na₂SO₄ and 6 M LiCl. The porous nature and tunable properties of MOFs despite its insulating nature make this composite as a suitable candidature for energy storage applications. FESEM analysis revealed a porous structure, facilitating enhanced electrolyte diffusion and charge storage mechanism. FTIR spectroscopy confirmed the interactions between MOF and MWCNTs leading to improved electrical conductivity. Raman spectroscopy confirmed structural integrity and defect states and stability of the composite material suitable as Supercapacitor. MOF showed crystalline in nature, with phase purity and strong interfacial interaction between Ni/Co-MOF and MWCNTs. For comparing the electrochemical behavior of the material in various electrolytes cyclic voltammetry, galvanostatic charge/discharge and electrochemical impedance spectroscopy techniques were employed. Among the tested electrolytes, 6 M KOH showed high conductivity and effective ion pathways approach so, better results were seen in this electrolyte of remarkable specific capacitance (1157.4 F g⁻¹ at 2 mV s⁻¹) and an impressive capacitance retention of 87.3 % at 4 A g⁻¹. Additionally, the composite exhibits excellent energy density of 205.90 Wh kg⁻¹ and a power density of 249.2 W kg⁻¹, which make composite suitable candidature for high-performance supercapacitors. Moreover, the outstanding coulombic efficiency of 136.67 % in KOH indicates excellent charge storage reversibility. The composite Ni—Co MOF/MWCNTs exhibits capacitive retention of is 87.3 % in 6 M KOH while in 1 M Na₂SO₄ and 6 M LiCl retention is 82.4 % and 79.7 % over 10,000 cycles These results show that 6.0 M KOH is the ideal aqueous electrolyte and concentration for MOFs based electrode materials.

CRediT authorship contribution statement

Priyanka Wadhwa: Writing – original draft, Methodology, Investigation, Data curation. **Pratap Singh:** Writing – original draft, Formal analysis, Data curation. **Robin Saini:** Writing – review & editing, Investigation, Formal analysis, Data curation. **Karuna Jain:** Writing – review & editing, Investigation, Formal analysis. **Neeraj Dilbaghi:** Writing – review & editing, Supervision, Resources, Methodology, Investigation, Conceptualization. **Rahul Kumar Dhaka:** Writing – review & editing, Methodology, Investigation, Formal analysis. **Manoj Kumar Singh:** Writing – review & editing, Methodology, Investigation, Formal analysis. **Sandeep Kumar:** Writing – review & editing, Visualization, Supervision, Resources, Investigation, Formal analysis, Conceptualization.

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

Data will be made available on request.

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