Article

Self-Supported Co$_3$O$_4$@Mo-Co$_3$O$_4$ Needle-like Nanosheet Heterostructured Architectures of Battery-Type Electrodes for High-Performance Asymmetric Supercapacitors

Yedluri Anil Kumar, Himadri Tanaya Das, Phaneendra Reddy Guddeti, Ramesh Reddy Nallapreddy, Mohan Reddy Pallavolu, Salem Alzahmi and Ihab M. Obaidat

Department of Physics, United Arab Emirates University, Al Ain 15551, United Arab Emirates; yedluri.anil@gmail.com
Department of Energy and Environment, United Arab Emirates University, Al Ain 15551, United Arab Emirates; s.alzahmi@uaeu.ac.ae
Centre of Advanced Materials and Applications, Utkal University, Vanivihar, Bhubaneswar 751004, India; himadridas@utkaluniversity.ac.in
Department of Physics, Sri Venkateswara Vedic University, Tirupati 517502, India; phaneendra369@gmail.com
School of Chemical Engineering, Yeungnam University, Gyeongsan 38541, Korea; rameshsun999@gmail.com
Department of Chemical & Petroleum Engineering, United Arab Emirates University, Al Ain 15551, United Arab Emirates

Correspondence: pmreddy@yu.ac.kr (M.R.P.); iobaidat@uaeu.ac.ae (I.M.O.)

These authors contributed equally to this work.

Abstract: Herein, this report uses Co$_3$O$_4$ nanoneedles to decorate Mo-Co$_3$O$_4$ nanosheets over Ni foam, which were fabricated by the hydrothermal route, in order to create a supercapacitor material which is compared with its counterparts. The surface morphology of the developed material was investigated through scanning electron microscopy and the structural properties were evaluated using XRD. The charging storage activities of the electrode materials were evaluated mainly by cyclic voltammetry and galvanostatic charge-discharge investigations. In comparison to binary metal oxides, the specific capacities for the composite Co$_3$O$_4$@Mo-Co$_3$O$_4$ nanosheets and Co$_3$O$_4$ nano-needles were calculated to be 814, and 615 C g$^{-1}$ at a current density of 1 A g$^{-1}$, respectively. The electrode of the composite Co$_3$O$_4$@Mo-Co$_3$O$_4$ nanosheets displayed superior stability during 4000 cycles, with a capacity of around 90%. The asymmetric Co$_3$O$_4$@Mo-Co$_3$O$_4$ AC device achieved a maximum specific energy of 51.35 Wh Kg$^{-1}$ and power density of 790 W kg$^{-1}$. The Co$_3$O$_4$@Mo-Co$_3$O$_4$ AC device capacity decreased by only 12.1% after 4000 long GCD cycles, which is considerably higher than that of similar electrodes. All these results reveal that the Co$_3$O$_4$@Mo-Co$_3$O$_4$ nanocomposite is a very promising electrode material and a stabilized supercapacitor.

Keywords: Co$_3$O$_4$@Mo-Co$_3$O$_4$ nanocomposite; binder free electrode; supercapacitor; hydrothermal; energy storage

1. Introduction

With broad applicability in the electronics, power systems, communication systems, and automobile sectors, supercapacitors have been recognized as being highly reliable among the numerous forms of energy storage devices. Supercapacitors exhibit high power densities and high charge storage abilities with long-term stability compared to batteries [1]. The cost-effective and less hazardous properties of supercapacitor components have motivated researchers to explore different electrode materials. Still, the practical usability of supercapacitors is limited due to their low energy densities for which battery-type electrodes are currently preferred. A wide range of transition mono-/multi-metallic oxides or hydroxides has been investigated as electrode materials for supercapacitors [2,3]. Among these, cobalt oxides have been found to possess high theoretical specific capacities [4].
The electrochemical properties of cobalt oxides can be improved by different strategies like tuning their morphology, doping with other metals, creating oxygen vacancies, etc. The tuning morphology is governed by the synthesis process, temperature, concentration, and reaction time. Among the various synthesis processes, the hydrothermal method is an old technique for synthesizing various nanomaterials. Interestingly, nanomaterials derived from hydrothermal methods with different shapes and sizes, dopants, core-shell, heterostructures, etc. have been found to be efficient for energy storage applications [5,6].

It has been reported that CoMoO$_4$ hexagonal 2D-nanosheets have high charge storage capabilities [7]. Such bimetallic oxides also have the advantage of the synergetic effect of both metals, where either both metals take part in redox reactions or one of them supports the electrochemical reaction of the other. Interestingly, oxygen vacancies are created in CoMoO$_{4-x}$ by hydrogenation of the hydrothermally obtained CoMoO$_4$ [8]. A theoretical study discovered that the oxygen vacancies have improved carrier density, thus increasing the electronic conductivity. The oxygen vacancy also acts as an active site for OH$^-$ intake and accelerates the charge transfer kinetics. Another strategy, i.e., doping the parent nanomaterial, has been widely explored due to the cost-effective approach to synthesis and ease of tuning the properties which it offers. For example, rare-earth metal (La, Nd, Gd, Sm) doping of Co$_3$O$_4$ synthesized by the polymer combustion method was employed for the study of the transfer of ions and electrons in supercapacitors [9]. Mo-doping of Co$_3$O$_4$ by various methods (sol-gel, electrodeposition, and hydrothermal) has been investigated as a means to synthesize potential electrode materials [10,11]. Shen et al. developed Mo-Co$_3$O$_4$ nanosheets as a battery-type electrode for supercapacitor applications and reported a specific capacity of 128.2 mAh/g at 1 A/g with 95% of capacity retention after long-term cyclings [12]. The experimental results were substantiated by theoretical calculations; it was shown that Mo-doping of Co$_3$O$_4$ modifies the bandgap and increases the electronic conductivity of the parent material, which enhances charge storage capability.

Recently, heterostructures have been designed as electrode materials for supercapacitors due to their extraordinary electrochemical performance and self-supported nanostructures with high structural and chemical stability [13]. A core-shell of hierarchical 3D NiCo$_2$O$_4$@ZnWO$_4$ was synthesized by the hydrothermal method for an all-solid-state symmetric supercapacitor (SSC) [14]. A multicomponent MnMoO$_4$/MnCo$_2$O$_4$ hybrid synthesized by a one-step hydrothermal method with urea as the reaction fuel was found to store ample charge with good reversibility [15]. Zhao et al. engineered Fe$_2$O$_3$ nanoneedle arrays with typical mesoporous structures and NiCo$_2$O$_4$/Ni(OH)$_2$ hybrid nanosheet arrays on SiC nanowire skeletons as asymmetric supercapacitors [16]. Binary heterojunction nanocomposites of CoTiO$_3$@Co$_3$O$_4$/N-single bond CNO matrix were established with excellent electrochemical properties [17]. Similarly, a hybrid, interconnected structure of nanoplates and nanowires of NiCo$_2$O$_4$ was found to have large surface area to support redox reactions [18]. A nanocomposite of needle-like Co$_3$O$_4$ and graphitic N-CNOS nanosheets was synthesized by a simple solvothermal and pyrolysis method [19]; it showed very high specific capacitance and good rate capability. Further, the asymmetric device with activated carbon (AC) showed good energy density and Coulombic efficiency. Such work proves that needle-like nanostructures along with nanosheets are appropriate electrodes for supercapacitors. There are many advantages of using nanomaterials, such as: (i) large surface area; (ii) synergistic charge storage; (iii) more electroactive sites exposed to the electrolyte; and (iv) time and cost-saving production.

In this work, a Co$_3$O$_4$@Mo-Co$_3$O$_4$ nanosheet composite heterostructure was synthesized by hydrothermal and pyrolysis method. As a result of the synergistic redox features between the Co$_3$O$_4$ nano-needles and Mo-Co$_3$O$_4$ nanosheets, the Co$_3$O$_4$@Mo-Co$_3$O$_4$ electrode displayed superior electrochemical activities with a specific capacity of 814 C g$^{-1}$ (1 A g$^{-1}$) and retention of 90% after 4000 long-cycles. In addition, an asymmetric supercapacitor (ASC) with continuous cycling stability was assembled utilizing Co$_3$O$_4$@Mo-Co$_3$O$_4$ and activated carbon (AC). The fabricated Co$_3$O$_4$@Mo-Co$_3$O$_4$/AC ASC displayed great electrochemical capacity, stability, and superior conductivity.
2. Experiment Procedure

2.1. Chemical Details

All chemicals were purchased from Sigma Aldrich and used without further processing. Cobalt nitrate hexahydrate (Co(NO$_3$)$_2$.6H$_2$O), sodium molybdate (NaMoO$_4$), and urea were used to synthesize the electrode material. N-Methyl-2-pyrrolidone (NMP, analytical grade), polyvinylidene fluoride (PVDF, analytical grade), nickel (Ni) foam, and activated carbon (AC, analytical grade) were used for electrode fabrication.

2.2. Synthesis of Co$_3$O$_4$ and Co$_3$O$_4$@Mo-Co$_3$O$_4$

The hetero-structure nanomaterial was synthesized via a facile hydrothermal method followed by low-temperature calcination. Pure precursors, i.e., cobalt nitrate, sodium molybdate, and urea, were used as-purchased. First, 2 mmol of Co(NO$_3$)$_2$.6H$_2$O (0.582 g), 1 mMol NaMoO$_4$ (0.206 g), and 10 mM urea (0.6 g) were completely dissolved in distilled water (25 mL) and ethanol (10 mL). Then, the 35-mL solution was transferred to a Teflon-lined autoclave for hydrothermal synthesis. The autoclave was subjected to heating to 120 °C and maintained for 10 h. Then, the autoclave was cooled to room temperature. The hydrothermal sample was washed with distilled water and ethanol to remove unreacted precursors or impurities, followed by drying at 60 °C. Finally, the obtained powder was calcinated at 350 °C for 3 h at a heating rate of 5 °C/min. Figure 1 presents a schematic view of the synthesis of the heterostructured Co$_3$O$_4$ nanoneedles and Mo-Co$_3$O$_4$ nano-petals. The low temperature used in the hydrothermal treatment allowed nucleation and the growth of nanoneedles and nanosheets to occur, while the post-annealing improved the crystallinity of the synthesized oxides.

![Schematic of Co$_3$O$_4$@Mo-Co$_3$O$_4$ needle-like nanosheets, synthesized by hydrothermal method.](image)

2.3. Characterizations

Detailed characterizations and an electrochemical analysis are available in the supporting file. In addition, the device fabrication procedure and calculation method of the specific capacity, energy, and power densities are provided and applied to the methods and calculations reported in previous literature [15,17,19–21].

2.4. Asymmetric Supercapacitor Preparation

For a three-electrode configuration, Co$_3$O$_4$ and Mo-Co$_3$O$_4$ coated on Ni foam were utilized as a working electrode, platinum wire as a counter electrode, and Ag/AgCl as a...
reference electrode, with 2.0 M KOH as the active electrolyte. For a two-electrode setup, Mo-Co$_3$O$_4$ coated on Ni foam was utilized as a positive electrode and activated carbon (AC) as a negative electrode, while Whatman filter paper—dipped in 2 M KOH solution and then placed between the positive and negative electrodes—was used as a separator. The mass-loading in the three-electrode setup was around 3 mg; in the two-electrode setup, an active mass of 8.7 mg was loaded onto the positive electrode (M) and 1 mg was loaded onto the negative electrode (AC). These values were chosen to balance the charge on both electrodes. The CV measurements for the ASC device were carried out in the potential range of −0.1 to 0.6 V at various scanning rates from 10 to 30 mV s$^{-1}$, whereas GCD characterizations were performed in potential ranges from 0 to 1.6 V at various current densities, i.e., ranging from 1 to 10 A g$^{-1}$. Moreover, EIS studies for both the two and three-electrode setups were carried out with an open circuit potential (OCP) ranging from 1 Hz to 100 kHz, with an AC perturbation of 5 mV.

In a three-electrode setup, the specific capacities were calculated from the GCD curves using the below equation:

$$C = \frac{I \cdot \Delta t}{m} \quad (1)$$

where $C$ is the specific capacity (C/g), $I$ indicates the discharge current (A), $\Delta t$ is the discharge time (s), and $m$ represents the mass of the active material (g). In the two-electrode setup, the specific capacitance (measured from GCD plots) of the active electrodes was calculated from the following equation:

$$C_s = \frac{I \cdot \Delta t}{m \cdot \Delta V} \quad (2)$$

To assemble the supercapacitor device, the charge stored on the positive and negative electrodes was described by $q^+ = q^-$. The mass balance of the positive and negative electrodes was estimated by:

$$\frac{m_+}{m_-} = \frac{C_{s-} x \Delta V^-}{C_{s+} x \Delta V^+} \quad (3)$$

Also, in the two-electrode setup, the energy density (Wh/Kg) and power density (W/Kg) were measured as follows:

$$E = \frac{1}{2} C_s (\Delta V)^2 \quad (4)$$

$$P = \frac{E}{\Delta t} \quad (5)$$

where $C_s$ is the specific capacitances (F/g), $\Delta t$ is the discharge time (s), $\Delta V$ is the operating voltage window (V), $m$ is the active mass of the working material (g), $E$ is the energy density (Wh/kg), and $P$ is the power density (W/kg).

3. Results and Discussion

The X-ray diffraction patterns of Co$_3$O$_4$ and Mo-Co$_3$O$_4$ were studied in the 2θ range of 10–80°, as presented in Figure 2a. The diffraction patterns demonstrated that the prepared heterostructure was polycrystalline, presenting several peaks which were consistent with Co$_3$O$_4$ planes. The diffraction patterns of the Co$_3$O$_4$ and Mo-Co$_3$O$_4$ heterostructure showed peaks at the (220), (311), (400), (511), and (440) planes, which corresponded to the cubic crystal structure of the Co$_3$O$_4$ phase. All of the planes matched with the JCPDS card no: 042-1467 [19]. The diffraction pattern showed no peaks corresponding to cobalt or molybdenum, indicating that no extra phases existed in the heterostructure. The XRD pattern of the Mo-doped Co$_3$O$_4$ heterostructure exhibited an additional peak at the (002) plane. Irrespective of the (002) plane, all the remaining planes showed pure Co$_3$O$_4$, indicating that no structural deformation had occurred in the host Co$_3$O$_4$ lattice upon Mo-doping.
This demonstrates that Mo ions were successfully substituted in the Co lattice positions in the Co$_3$O$_4$ matrix.

Rietveld refinement was also used to determine the presence of Mo in the Co$_3$O$_4$ lattice for the Co$_3$O$_4$@Mo-Co$_3$O$_4$ heterostructure. In this analysis, R weighted profile ($R_{wp}$), R profile ($R_p$), R structure factor, R Bragg factor ($R_{Bragg}$), and goodness of fit (GOF) structural parameters were evaluated (as shown in Figure S1) using the EXPO software. The unit cell parameters were also calculated using the Rietveld refinement results. Table 1 shows the estimated Rietveld refinement parameters, including $R_p$, $R_{wp}$, GOF, R structure factor, $R_{Bragg}$, and the unit cell parameters. The quality of Mo substitution in the Co$_3$O$_4$ matrix can be determined from the GOF value, which is 0.805.

Table 1. Estimated lattice structure parameters and refinement parameter values from Rietveld refinement of Co$_3$O$_4$@Mo-Co$_3$O$_4$ heterostructure.

| Unit Cell Parameters | Value |
|----------------------|-------|
| a, (Å)               | 8.08  |
| b, (Å)               | 8.08  |
| c, (Å)               | 8.08  |
| α, (°)               | 90    |
| β, (°)               | 90    |
| γ, (°)               | 90    |
| Cell volume (Å$^3$)  | 528.24|
| Density (g/cm$^3$)   | 6.05  |
Table 1. Cont.

| Unit Cell Parameters |
|----------------------|
| Crystal system and Space group number | Cubic & (Fd-3m, 227) |

| Structure parameters |
|----------------------|
| Atoms | 130 |
| Bonds | 168 |
| Polyhedra | 34 |

| Refinement parameters |
|-----------------------|
| $R_p$ | 1.762 |
| $R_{wp}$ | 2.216 |
| Goodness of fit (GOF) | 0.805 |
| R-Structure factor | 4.68 |
| R-Bragg factor | 6.89 |

Table 2 displays the site occupancy values of ions distributed with the corresponding fractional coordinate values. $\text{Co}_3\text{O}_4$ contains three Co sites (Co1, Co2, Co3) and two O sites (O1 and O2). The unit cell lattice parameters are included in Table 1. Further, the crystal structure and atomic bonding in $\text{Co}_3\text{O}_4$ were evaluated using the Vesta software. $\text{Co}_3\text{O}_4$ demonstrated a cubic crystal structure with space group Fd-3m (space group number: 227), with 130 atoms distributed with 168 bonds. Table 2 lists the structural parameters, while Figure 2 depicts the crystal structure.

| Table 2. Site occupancies of various ions along with their fractional coordinates. |
|-------------------|---|---|---|---|---|---|
| Element | X | Y | Z | Occupancy | Site | Sym. |
|-------|----|---|---|-----|------|-----|
| O1 | 0.14000 | 0.14000 | 0.14000 | 1.000 | 16e | 0.3 m |
| O2 | 0.60000 | 0.60000 | 0.60000 | 1.000 | 16e | 0.3 m |
| Co1 | 0.75000 | 0.75000 | 0.75000 | 1.000 | 4d | −43 m |
| Co2 | 0.00000 | 0.00000 | 0.00000 | 1.000 | 4a | −43 m |
| Co3 | 0.37500 | 0.37500 | 0.37500 | 1.000 | 16e | 0.3 m |

Figure 2b shows Raman spectra of the $\text{Co}_3\text{O}_4$ and $\text{Co}_3\text{O}_4@\text{Mo-Co}_3\text{O}_4$ heterostructure. The Raman spectrum of intense peaks showed the Mo-O-Co stretching vibrations for $\text{Co}_3\text{O}_4@\text{Mo-Co}_3\text{O}_4$. The intense peaks in both samples may have arisen due to the vibrations of Co-O bonds representing the breathing mode of point phonons in the $A_{1g}$ symmetry [5]. Several small peaks appeared due to the scattering of the $F_{2g}$ or $E_g$ phonons [7]. These bands can be integrated into Mo-O-Mo, Mo-O, and MoO$_4$ vibrations [8]. The results suggest that the synthesis of the $\text{Co}_3\text{O}_4@\text{Mo-Co}_3\text{O}_4$ heterostructure composite was successful.

In addition, FTIR analysis was performed on the $\text{Co}_3\text{O}_4@\text{Mo-Co}_3\text{O}_4$ needle-like nanosheet heterostructure for additional phase evolution, as presented in Figure S2. This is the first reported FTIR analysis of Mo-doped $\text{Co}_3\text{O}_4$ in a supercapacitor-related publication. The sharp peaks at 560 and 665 cm$^{-1}$ correspond to pure $\text{Co}_3\text{O}_4$, comprising Co-O stretching vibrations [22]. These two bands confirm the presence of $\text{Co}_3\text{O}_4$, which is related to the $\text{O}B_3$ vibration ($\text{B} = \text{Co}^{3+}$ in an octahedral hole); the other band is related to the $\text{ABO}_3$ vibration ($\text{A} = \text{Co}^{2+}$ in a tetrahedral hole) [23]. The small peaks at around 3425 and 1645 cm$^{-1}$ resulted from the O-H groups [24]. The shift could be observed for the Mo-doped $\text{Co}_3\text{O}_4$, and was attributed to a change in the surface area as well as a surface defect due to the doping [25]. The peak at 1058 cm$^{-1}$ belonged to the carbonate groups which resulted from air contamination during the reaction of oxide with Co$_2$ [26].

The chemical composition and valance state of the $\text{Co}_3\text{O}_4@\text{Mo-Co}_3\text{O}_4$ needle-like nanosheet heterostructure were analyzed using X-ray photoelectron spectroscopy (XPS), revealing the oxidation state of the transition metal ion. Figure 2c displays the spectra of Mo-Co$_3$O$_4$, showing Mo, Co, and O peaks in addition to C. The core-level photoelectron spectra of Mo3d, Co2p, and O1s are presented in Figure 2d–f. The Mo3d core transition
was considered by a doublet due to the spin-orbit coupling resulting from the 3d_{5/2} and 3d_{3/2} components. The binding energies of Mo3d_{5/2} and Mo3d_{3/2} were 231.92 ± 0.1 eV and 235.06 ± 0.1 eV, respectively. The local structure of the Mo atoms in the CoO_{2} lattice offered information about its chemical state and was primarily responsible for these peak placements. The detected binding energy values of Mo differed from those of Mo-O-related compounds, indicating that the Mo cations had been perfectly substituted in the Co sites of the cubic structure.

Figure 2c shows two distinct peaks at 780.15 ± 0.1 eV and 795.64 ± 0.1 eV, which belong to 2p_{3/2} and 2p_{1/2}, respectively. The energy difference between the Co 2p_{3/2} and 2p_{1/2} splitting was 15.49 eV, which indicated the existence of Co^{2+} and corresponded to the existence of CoO_{3}. It can be noted that the binding energy difference ΔE between the Co2p_{1/2} and Co2p_{3/2} (15 eV) observed in the complex was equal to that found for Co(III), which was in agreement with the reported value [27]. The peak detected at 530.26 ± 0.1 eV was attributable to O1s linked to Co and Mo atoms in the lattice oxygen (see Figure 2d). Because the activation energy for oxygen diffusion is substantially higher than that for interstitial Co atoms and Mo^{6+} ions, enough oxygen atoms from the atmosphere can diffuse into the CoO_{2} lattice to fill up the new oxygen vacancies created by the increase of Co(III) and Mo^{6+} ions during MoCoO_{3} development. The existence of Co and O in XPS spectra is consistent with the XRD patterns.

The morphology of CoO_{3}@Mo-CoO_{3} was characterized by FESEM, as shown in Figure 3. The one-pot hydrothermal synthesized CoO_{3}@Mo-CoO_{3} was found to be heterostructured. It is worth mentioning that the heterostructures composed of the monolayer CoO_{3} and some Mo-CoO_{3} nanosheets demonstrated eminent structural formation. The images in Figure 3a–f show the CoO_{3}@Mo-CoO_{3} at different magnifications. A bundle of nanoneedles of CoO_{3} was arranged over a bud to give a flower-like nanostructure, while the Mo-CoO_{3} nanosheets were stuck on/in the nanoneedles. The fact that the self-supported heterostructure formed without the addition of any surfactant or template is quite interesting. The CoO_{3} and Mo-CoO_{3} heterostructures exhibited excellent metallic characteristics and great structural stability, delivering better electronic conductivity and structural integrity than pristine composites. Moreover, self-assembled particles reduce the surface energy, enhancing the stability of the structure. Within the hierarchical heterostructures, both core and shell are active materials, and the core-shell heterostructures enable easy access to electrolytes. Therefore, both of them can effectively contribute to the capacity. Figure 3g shows the EDS spectra obtained for the elemental studies, whereas Figure 3h–j shows the elemental mapping for the Mo, Co, and O present in the CoO_{3}@Mo-CoO_{3} needle-like nanosheet heterostructure. It is expected that the architecture can be beneficial for boosting electrochemical performance.

HRTEM images of the CoO_{3}@Mo-CoO_{3} heterostructure are depicted in Figure 4, where the resolutions in a, b, and c are 50, 10, and 5 nm, respectively. Figure 4a,b clearly convey that there are different shapes of nanoneedles, i.e., a flower and small sheets attached to it. It was observed that the wide exposed nanoneedles in flower form provided space for the small sheets inside them, as well as sharp tips to hold nanosheets. Thus, the hydrothermal growth of the heterostructured CoO_{3} nanoneedles and Mo-CoO_{3} nanoplates resulted in the creation of interesting nanostructured electrode materials. The highest resolution image (Figure 4c) shows fringes, where the SAED pattern (inset in Figure 4c) confirms the highly crystalline nature of the hetero-structured nanomaterials. The precise spacings of 0.24, 0.29, and 0.46 nm were well-matched with the (311), (220), and (111) planes of Mo-CoO_{3}. The well-organized rings and dots seen in the SAED pattern prove the crystallinity nature of the electrode materials that could be beneficial in structure retention for long-term stability. There is no doubt that such an architecture would support efficient electrochemical performance in supercapacitor applications.
Figure 3. (a–f) FE-SEM images of Co$_3$O$_4$@Mo-Co$_3$O$_4$ needle-like nanosheet heterostructure at different magnifications, (g) EDS spectra: inset mapping image of Co$_3$O$_4$@Mo-Co$_3$O$_4$, (h) elemental map of Mo, (i) elemental map of Co, and (j) elemental map of O.

Figure 4. (a,b) TEM images at different magnifications, (c) high-resolution TEM image of Co$_3$O$_4$@Mo-Co$_3$O$_4$ needle-like nanosheet heterostructure: inset SAED pattern.

3.1. Electrochemical Properties of Electrode Materials

The hydrothermally obtained heterostructures were tested for three-electrode system electrochemical performance in 2M KOH electrolytes. Figure 5 illustrates a comparison of the Co$_3$O$_4$ and Co$_3$O$_4$@Mo-Co$_3$O$_4$ needle-like nanosheet heterostructure electrodes. It was found that the doping of Mo into Co$_3$O$_4$ enhanced the electrochemical properties, such as peak current and discharge time (Figure 5a,b). Notably, the cyclic voltammetry (CV) curves and the galvanic charge-discharge (GCD) curves demonstrated that doping did not shift the redox peaks of the Co$_3$O$_4$. This indicated that Co$_3$O$_4$ undergoes redox reactions while Mo facilitates the electrochemical performance of Co$_3$O$_4$. The CV curves in the potential window of $-0.1$ to $0.6$ V at different scan rates, i.e., $10$–$30$ mV/s, obtained for Co$_3$O$_4$ and the Co$_3$O$_4$@Mo-Co$_3$O$_4$ heterostructures, are shown in Figure 6c,d. At each scan rate, clear oxidation and reduction peaks ($0.35$ V and $0.2$ V) were found in the same place, with an increase in the current density with increasing scan rate. Figure 5e,f presents the GCD profiles in a potential window of $0$ to $0.45$ V at different current densities, i.e., $1$–$10$ A/g, obtained for Co$_3$O$_4$ and the Co$_3$O$_4$@Mo-Co$_3$O$_4$ heterostructure. The battery-type behavior is clearly visible in the plateau-like charge/discharge pattern. The Co$_3$O$_4$ and Co$_3$O$_4$@Mo-Co$_3$O$_4$ heterostructure revealed similar humps, indicating the occurrence of redox reactions due to cobalt, where Mo-Co$_3$O$_4$ has a higher discharge time than Co$_3$O$_4$. The Mo atoms did not show redox activity during charge/discharge reactions but promoted electrochemical performance. The calculated specific capacity is given in Figure 5g. The faradaic reactions for Co$_3$O$_4$ are given below [28]:

\[
\text{Co}_3\text{O}_4 + \text{H}_2\text{O} + \text{OH}^- \rightarrow 3\text{CoOOH} + \text{e}^- (6)
\]

\[
\text{CoOOH} + \text{OH}^- \rightarrow \text{CoO}_2 + \text{H}_2\text{O} + \text{e}^- (7)
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\]

Figure 5. (a,b) Comparison plots of CV at 10 mV/s scan rate and GCD at 1 A/g current density for Co$_3$O$_4$ and the Co$_3$O$_4$@Mo-Co$_3$O$_4$ heterostructure, (c,d) CV curves at scan rates of 10–30 mV/s, (e,f) GCD curves at current densities of 1–10 A/g, (g) calculated specific capacity values from GCD curves, (h) Nyquist plot of Co$_3$O$_4$ and the Co$_3$O$_4$@Mo-Co$_3$O$_4$ heterostructure, (i) capacitance retention over 4000 GCD cycles; inset: ten consecutive GCD cycles.
The advantage of Mo-doping is to facilitate the electrochemical ability. The heterostructure formed by the addition of Mo improved the charge storage capacity by 30%. The pristine Co$_3$O$_4$ electrode exhibited a specific capacity of 615 C/g (1464 F/g), whereas the Co$_3$O$_4$@Mo-Co$_3$O$_4$ needle-like nanosheet heterostructure had a specific capacity of 814 C/g (1850 F/g). Besides Mo-doping, the enhanced electrochemical performance could be attributed to the heterostructure architecture of the obtained nanomaterials. The Mo-Co$_3$O$_4$ flower-like nanosheets provided a large area, leading to better electrolyte diffusion into the electrodes. In addition, the Mo-Co$_3$O$_4$ flower-like nanosheets provided an active electrochemical surface for redox reactions. The self-supported structure comprised a large...
surface area for charge storage and fast electron transfer reactions. The advantages of this morphology are reflected in the Nyquist plot given in Figure 5h. The solution resistance was found to be 1 Ω and 0.65 Ω for Co₃O₄ and for the Co₃O₄@Mo-Co₃O₄ heterostructure, respectively (inset in Figure 5h). However, the reduced resistance would have increased the charge kinetics during the electrochemical process. Further, the stability test for 4000 cycles of continuous charge/discharge process in the KOH electrolyte was done with the Co₃O₄@Mo-Co₃O₄ heterostructure electrode. Even at the 4000th cycle, around 90% capacity retention was observed for the Co₃O₄@Mo-Co₃O₄ electrode. The inset of the last 10 similar GCD cycles corroborates the structural stability of the Co₃O₄@Mo-Co₃O₄ heterostructure electrode during long-term cycling. Thus, the excellent morphology and crystallinity of the Co₃O₄@Mo-Co₃O₄ needle-like nanosheet heterostructure electrode indicate that it is a very promising electrode material for supercapacitor applications.

3.2. Electrochemical Properties of a Co₃O₄@Mo-Co₃O₄//AC Device

For practical applications, the Co₃O₄@Mo-Co₃O₄ heterostructure electrode was assembled with an AC electrode in a KOH electrolyte as an asymmetric supercapacitor, as represented in Figure 6a. The comparative CV curves of the negative AC and positive Co₃O₄@Mo-Co₃O₄ electrodes are presented in Figure S1. The asymmetric (Co₃O₄@Mo-Co₃O₄//AC) device potential window was optimized, as shown in Figure 6b,c. The CV curves in Figure 6b at 80 mV/s and the GCD profile at a current density of 3 A/g (Figure 6c) were made at different potential windows. The optimum potential window for the constructed device was found to be 0–1.6 V. The CV curves for the device were obtained at different scan rates, i.e., 50–100 mV/s, and GCD curves at various current densities, i.e., 1–10 A/g, as demonstrated in Figure 6d,e.

The calculated specific capacity for the Co₃O₄@Mo-Co₃O₄//AC device is shown in Figure 6f. It showed a maximum capacitance of 154.6 F g⁻¹ at a current density of 1 A g⁻¹. The superior supercapacitor performance might be accredited to the strong self-supported structure. The Ragone plot (Figure 6g) illustrated the energy and power density of the asymmetric Co₃O₄@Mo-Co₃O₄//AC device. The device exhibited an energy density of 51.35 Wh/kg at a power density of 790 W/kg. The values of Co₃O₄@Mo-Co₃O₄//AC device from the GCD are shown in Table 3, affirms improved capacitive performance of fabricated Co₃O₄@Mo-Co₃O₄//AC device compared to previously reported works.

Table 3. Various electrochemical properties of Co₃O₄-related materials compared to previous reports.

| Electrode        | Electrolyte | Specific Capacitance | Retention Rate | Energy Density (Wh kg⁻¹) | Power Density (W kg⁻¹) | Ref.       |
|------------------|-------------|----------------------|----------------|--------------------------|------------------------|-----------|
| Mn@Co₃O₄         | 2M KOH      | 773 F g⁻¹            | 73.9%/5000 cycles | NA                       | NA                     | [29]      |
| Mn-Co₃O₄/NF      | 2M KOH      | 668.4 F g⁻¹          | 104%/10,000    | 10.63                    | 14,700                 | [30]      |
| V-Co₃O₄          | 3M KOH      | 1593 F g⁻¹           | NA             | 66.88                    | 240                    | [31]      |
| Fe-Co₃O₄         | 6M KOH      | 767.9 C g⁻¹          | 90%/4000       | 37                       | 750                    | [32]      |
| Cr, Sn- Co₃O₄    | 3M KOH      | 1413.56 Fg⁻¹         | 89.41%/3000    | NA                       | NA                     | [33]      |
| Ce-Co₃O₄         | 3M KOH      | 1309.6 F g⁻¹         | 90.86%/2000    | NA                       | NA                     | [34]      |
| Mo-Co3O4//AC     | 2M KOH      | 1850 F g⁻¹           | 90%/4000       | –                        | –                      | This      |
| Mo-Co3O4//AC     | 2M KOH      | 148 F g⁻¹            | 89%/4000       | 51.4                     | 790                    | Work      |

The EIS study summarized in Figure 6h reveals minimal increase in solution resistance, even after 4000 cycles of charge/discharge. As shown in Figure 6i, the high retention (89%) also proved the long-term durability of the asymmetric device. Thus, the Co₃O₄@Mo-Co₃O₄//AC device is promising for use in advanced electronics. Such significant electrochemical outcomes could be attributed to the crystallinity and morphology of the Co₃O₄@Mo-Co₃O₄ needle-like nanosheet heterostructure electrode, the self-supported structure with good mechanical and chemical stability, and the numerous nanoneedles, which offer enough surface area and active sites for electrochemical reactions and elec-
4. Conclusions

A novel Co$_3$O$_4$@Mo-Co$_3$O$_4$ nanosheet composite for supercapacitor applications was synthesized and its physical/electrochemical characteristics were investigated. The Co$_3$O$_4$@Mo-Co$_3$O$_4$ nanosheet composite achieved a superior specific capacity of 814 C g$^{-1}$ at 1 A g$^{-1}$ and capacity retention of 90% with a good rate capability. The asymmetric SC fabricated using this composite material achieved a capacitance of 154.6 F g$^{-1}$ at 1 A g$^{-1}$, a specific energy of 51.35 Wh Kg$^{-1}$, and a specific power of 790 W kg$^{-1}$. Moreover, the Co$_3$O$_4$@Mo-Co$_3$O$_4$/AC device possesses superior rate capabilities and long cycles, with 89.7% of the starting capacitance remaining after 4000 continuous cycles at 2 A g$^{-1}$. From this work, it may be concluded that the nanocomposite Co$_3$O$_4$@Mo-Co$_3$O$_4$ nanosheets coated over a Ni foam skeleton displayed superior capacities and could be considered for use in ultra-capacitor devices in the future.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/nano12142330/s1. Figure S1. The Rietveld refinement pattern of Co$_3$O$_4$@Mo-Co$_3$O$_4$ heterostructure; Figure S2. FTIR spectra of Co$_3$O$_4$ and Co$_3$O$_4$@Mo-Co$_3$O$_4$ composite; Figure S3. CV curves of two electrodes positive and negative.

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