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Synthesis of Co(OH)$_2$/CNTs nanocomposite with superior rate capability and cyclic stability for energy storage applications

Imran Shakir$^1$, Zeyad Almutairi$^{1,2,3}$, Sahar Saad Shar$^4$ and Ayman Nafady$^5$

$^1$ Sustainable Energy Technologies Center, Saudi Arabia, P O Box 800, Riyadh 11421, Saudi Arabia
$^2$ Mechanical Engineering Department, College of Engineering, Saudi Arabia, P O Box 800, Riyadh 11421, Saudi Arabia
$^3$ K.A.CARE Energy Research and Innovation Center at Riyadh, Saudi Arabia, P O Box 800, Riyadh 11421, Saudi Arabia
$^4$ Deanship of Scientific Research, Saudi Arabia, P O Box 800, Riyadh 11421, Saudi Arabia
$^5$ Chemistry Department, College of Science King Saud University, Riyadh, Saudi Arabia, P O Box 800, Riyadh 11421, Saudi Arabia

E-mail: mshakir@ksu.edu.sa

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Abstract

The good rate capability and longer cyclic performance are the two key features electrochemical capacitors that are highly dependent on the electrochemical stability, structure, electrical conductivity, composition, and nature of the charge storing–mechanism involved by its electrodes. Herein, we fabricated layered Co(OH)$_2$ and their nanocomposite with carbon nanotubes (CNTs, 5%) via a two-step approach for electrochemical applications. The as-prepared nanocomposite based electrode displays good specific capacitance (Cs), negligible capacity fade, and promising rate capability on electrochemical tests via a three-electrode configuration. More precisely, the nanocomposite based electrode showed Cs of 802 Fg$^{-1}$ at 0.5 Ag$^{-1}$ and lost just 3.8% of its initial capacitance (at 1st cycle) after 5000 cyclic tests. Furthermore, the nanocomposite electrode lost around 14% of its initial capacitance on increasing the current density from 0.5 to 5 Ag$^{-1}$ that reveals its novel rate capability. The observed superior electrochemical aptitude of the fabricated nanocomposite is credited to the layered nanoarchitecture of the Co(OH)$_2$ and CNTs matrix. The CNTs-matrix, because of their lower properties, performs multiple roles to improve the supercapacitive performance of the whole composite. Firstly, they accelerate the charge transfer within the nanocomposite matrix due to its higher electrical conductivity. Secondly, they facilitate mass transport due to its hollow structure. Thirdly, they sandwich between the layers of Co(OH)$_2$ and suppress the stacking process. Fourthly, the added CNTs itself act as a capacitive supplement and further improve the specific capacitance of the nanocomposite. Finally, CNTs buffers the whole nanocomposite against the volume expansion during the continuous cyclic tests. The electrochemical and structural stability of Co(OH)$_2$/CNTs sample was also evaluated by EIS and PXRD characterizations after electrochemical tests. The acquired result showed that fabricated nanocomposite has great potential for advanced energy storage applications.

1. Introduction

Currently, environmental pollution and energy crisis are the two main concerns that are getting worst throughout the world due to industrialization and accelerating population growth. These ever-increasing problems provoke the current electrochemical researchers (ECRs) to develop eco-friendly and highly efficient energy storage devices. Usually, Lithium-ion- batteries (LIBs), fuel cells (FCs), conventional capacitors (CCs), and electrochemical capacitors (ECCs) are employed for energy production, conversion, and storage purposes. Among the aforementioned devices, ECCs have drawn the considerable attention of the current ECRs because of their excellent power density ($\geq 10$ kW kg$^{-1}$), good safety, short charging-time (few seconds), and longer cyclic life ($>10^6$).
Based on the charge accumulation processes, the ECCs have been classified into electrical-double-layer capacitors (EDLCs) and pseudocapacitors (PsCs) [1, 2]. The EDLCs store energy by accumulate charge (ions of electrolyte) via simple physical adsorption at their electrode surface [3]. As specific capacitance (Cs) of the EDLCs mainly depends upon the surface area of their electrodes, hence high surface area carbonaceous materials are considered more suitable electrode material [4]. The EDLCs deliver energy at higher rates (higher power density) as the charge-storage process is simply physical and involve the exposed surface of the electrode only [5]. Unfortunately, these capacitors (EDLCs) offer low Cs and energy density, usually from 80–300 F g⁻¹, as the charge storage mechanism is potential independent, and the larger bulk of the electrode have no contribution toward the total capacitance. In contrast, the PsCs involve reversible faradic (redox) reaction at the surface and subsurface (few nm below the surface) of their electrodes to deliver higher Cs at considerable rates [6].

The redox-active materials such as conducting polymers (CPs), oxide, sulfides, and hydroxides of transition metals are considered suitable electrode material for PsCs applications [7–10]. Nevertheless, the cyclic stability and rate capability of the CPs is inferior to that of transition-metal based redox-active materials [11].

The cobalt-based compounds are highly efficient electrode materials for PsCs applications due to their higher theoretical capacitance (Cth, 3458 F g⁻¹), ecofriendly nature, variable oxidation states, and facile preparation process. Recently, the oxide and hydroxide of cobalt and their nanocomposite with carbonaceous materials have been investigated widely as a positive electrode for PsCs applications. The cobalt hydroxide (Co(OH)₂) has drawn much attention from the modern electrochemical researchers due to its higher redox-activity, higher accessible surface area, good chemical stability, low-cost, speedy ion transport, and 2D layered structure with interlayer spacing and their well-defined electrochemical redox activity [12, 13]. As Cs of the electrode material directly depends upon its electrochemical active-surface area, so 2D layered Co(OH)₂, because of their higher electrochemical active-surface area, shows superior capacitive performance.

Unfortunately, the lower electrical conductivity, narrow potential window, and poor structural stability of the Co(OH)₂ badly affect its power density, Cs, and cyclic stability [14]. The researchers have developed various strategies to improve the electrical conductivity and widen the potential window of the Co(OH)₂. Zhao et al. prepared Mn-doped Co(OH)₂ nanosheets by the hydrothermal route. Their prepared doped sample electrode exhibit the Cs of 1915 F g⁻¹ (1 Ag⁻¹) and retained 93.5% of this capacitance after 5000 cyclic experiments [13]. The nanocomposite of Co(OH)₂ with other transition metal-hydroxides and oxides such as Co(OH)₂/Ni(OH)₂ [15], Mn₂O₃/Ni(OH)₂ [16], Co(OH)₂/ZnO [17], and CoOOH/Co(OH)₂ has been investigated to tune the electrical conductivity and increase the potential window. Jiang et al. synthesized Co(OH)₂/MXene nanocomposite via deposition precipitation route. Generally, the mixing of highly conductive substrates (graphene, MXene, CNTs, etc) with nanostructured Co(OH)₂ is a superior strategy as added conductive matrix not only tune the electrical conductivity of the material but also act as a capacitive supplement [18]. Their fabricated nanocomposite exhibit outstanding capacitance retention (99% after 1000 cyclic tests) and rate capability [19]. Zhao et al. prepared Co(OH)₂/graphene nanocomposite and decorated it directly on the Ni-foam via electro-deposition approach. Their fabricated binder-free electrode delivers Cs of almost 694 F g⁻¹ at 2 Ag⁻¹ and keeps almost 92% of their initial Cs after 3000 cyclic experiments [20]. Cheng et al. fabricated Co(OH)₂/CNTs/r-GO ternary nanocomposite via electro-deposition method. Their fabricated nanocomposite shows the Cs of 310 F g⁻¹ at 1 Ag⁻¹ and lost 30% of this capacitance after 1500 cyclic experiments [21]. Moreover, the added conductive-matrix, because of its higher electrical conductivity, unique structure, and good chemical stability, also suppress the agglomeration and volume expansion of the nanocomposite electrode during successive charge/discharge experiments [22].

Among the commonly used conductive matrix, CNTs with higher aspect-ratio are very promising candidates because of their novel electrical, mechanical, and thermal properties. The 2D morphology of the Co(OH)₂ nanomaterial improves its contact area with the added matrix that results in fast charge transport, speedy diffusion, and maximum utilization of the surface area [23]. Among the various carbonaceous materials, the one-dimensional CNTs are being explored extensively because of their higher aspect ratio and good mechanical and electrical properties [14].

Herein, we synthesized Co(OH)₂ nanoflakes via a simple co-precipitation route and form their nanocomposite with 5% CNTs via ultra-sonication approach. The fabricated samples were decorated on a stainless steel substrate and used the prepared electrode as a working electrode in a three-electrode configuration. The electrochemical experiments were carried to investigate the cyclic stability, specific capacitance, rate-capability, and kinetics properties of the prepared samples.
2. Experimental section

2.1. Reagents
Analytical grade hydrated cobalt (II) sulphate (Co(SO₄)₂·7H₂O, 99%), and potassium hydroxide (KOH, 98%) were purchased from AnalaR. The absolute alcohol (C₂H₅OH, >99%) and hydrazine hydrate (H₄N₂O₂, >99%) were purchased from Fisher chemicals. The aqueous dispersion of the CNTs having the concentration of 1 g/1 l was purchased from the XFNANO supplier.

2.2. Material synthesis
All purchased raw materials were used as received. The layered cobalt-hydroxide (LCO–OH) was prepared by simple co-precipitation rout by following the recently published method of Wang et al [24]. In a typical synthesis, CoSO₄·7H₂O (0.56 g, 2 mmol) was dissolved in distilled water (DW, 70 ml) to get the dark-red aqueous solution. The pH of the dark-brown aqueous solution was 5.65. Afterward, the N₂H₄·H₂O (80%) was taken in the burette and added drop-wise into the stirring aqueous-solution of the CoSO₄·7H₂O. The N₂H₄·H₂O was added until the pH of the final mature increased up to 7.7. The resulted solution was kept on stirring for an additional 8 h. After 8 h of stirring, the bluish precipitates were filtered and washed many times with water and ethanol. Finally, the bluish precipitates were dried at 60 °C for 12 h. Following chemical changes are expected during the synthesis process:

\[ \text{N}_2\text{H}_4 + \text{H}_2\text{O} \rightarrow \text{N}_2\text{H}_5^+ + \text{OH}^- \]  

\[ \text{N}_2\text{H}_5^+ + \text{H}_2\text{O} \rightarrow \text{N}_2\text{H}_6^{2+} + \text{OH}^- \]  

\[ \text{Co}^{2+} + 2\text{OH}^- \rightarrow \text{Co(OH)}_2(\text{bluish ppt}) \]  

2.3. Fabrication of Co(OH)₂ nanocomposite with 5% CNTs
The nanocomposite of the Co(OH)₂ with 5% CNTs was synthesized via the ultras-sonication approach. Firstly, dried precipitates of Co(OH)₂ (47.5 mg) were added into the distilled water (80 ml) and placed the mixture in the sonication machine for 30 min at room temperature. Secondary, about 2.5 ml from the aqueous dispersion of CNTs (1 g/1 l) was added into the above mixture and placed it in the sonication machine for a further 30 min. After sonication-operation, the homogeneous mixture was evaporated at 90 °C for 10 h to get the solid-product of Co(OH)₂/CNTs.

2.4. Physical characterizations
The morphological and structural properties of the fabricated samples were investigated via scanning electron microscopy (SEM, Hitachi/SU8020). Crystalline state and surface chemical analysis of the prepared samples were completed via P-XRD (Rigaku-Ultima) and FT-IR (PerkinElmer-spectrum) characterizations. The thermal stability of Co(OH)₂ and % of CNTs in nanocomposite was examined by TGA analysis (TA-Q50). The electrical-conductivity behavior of the Co(OH)₂ and Co(OH)₂/CNTs was investigated via the I–V test (Keithley 6487).

2.5. Working electrode preparation
The mixture of ethanol and active-material was grounded finely to form the slurry. The slurry was spread over the piece of stainless steel (SS, 2 cm × 3 cm). The stainless-steel substrate own to its superior electrical conductivity (1.45 × 10⁶ sm⁻¹) offers negligible contact resistance at the electrode-analyte interface. The sample decorated stainless-steel electrode was dried for 5 h at 70 °C. The weight of loaded analyte/active material was 2.5 mg that was determined by weighing the pristine stainless-steel substrate and dried-sample loaded stainless steel substrate. The dried-sample electrodes were kept in 3 M KOH electrolyte for 6 h to obtain the highly consistent results.

2.6. Electrochemical characterizations
All electrochemical experiments were performed at room temperature in an aqueous electrolyte (3 M KOH). In half-cell experiments, sample-decorated stainless steel works as a working electrode, while Ag/AgCl and Pt-foil serve as a reference and auxiliary electrode, respectively. The cyclic voltammetry (CV) experiments were performed within the potential range from 0 V to 0.6 V at varying scan rates (5–80 mV s⁻¹). The charge/discharge experiments were also performed in the potential-range similar to CV experiments at varying current density (0.5–5 A g⁻¹). The response of the fabricated sample to the alternating voltage (AC) was also investigated via EIS experiments in a frequency range from 0.1 MHz to 0.01 Hz. The specific capacitance (Cs) of the fabricated samples was calculated via their CV and CCD results by using equations (4) and (5), respectively [25, 26].
observed due to the diffractions from the (002) diffraction of the carbonaceous materials [28]. In our case, the existence of broad hump indicates the existence of CNT (carbonaceous material). Moreover, the presence of all characteristics peaks of Co(OH)\(_2\) and CNT in the PXRD of Co(OH)\(_2\)/CNT NCs indicated that mixing of CNT with Co(OH)\(_2\) is just physical. The grain size (D) of the synthesized sample was determined by using the following modified Scherrer equation.

$$\ln \beta = \ln \frac{1}{\cos \theta} + \ln \frac{K\lambda}{D}$$  \hspace{1cm} (6)

The value of \(\ln(\beta)\) and \(\ln \frac{1}{\cos \theta}\) were determined from the FWHM and peak position of the diffraction peaks as illustrated in table 1. The equation (6) is a straight-line equation whose y-intercept (\(\ln \frac{K\lambda}{D}\)) was determined by plotting a graph between \(\ln(\beta)\) (on the y-axis) and \(\ln \frac{1}{\cos \theta}\) (on the x-axis) as depicted in figure 2(a).

The average grain size, calculated from modified Scherrer-equation, was come to be 12.4 nm. Apparently, the sharp and high-intense nature of the diffraction peaks reveals the good crystallinity of the fabricated product. More precisely, the % crystallinity of the fabricated product was also determined via the following relationship [29]:

$$C_p = \frac{Q_a + Q_i}{2m\Delta V}$$  \hspace{1cm} (4)

$$C_p = \frac{i \times \Delta t}{\Delta V}$$  \hspace{1cm} (5)

3. Result and discussion

3.1. Physical characterizations

Fabrication of nanostructured Co(OH)\(_2\) and its nanocomposite (NCs) with CNTs was confirmed by FE-SEM analysis. Figure 1 illustrates the FE-SEM micro-images of the fabricated products.

The micro-image of Co(OH)\(_2\) (figure 1(a)) at 30 000 magnifications reveals that 2D nanoflakes of the fabricated sample arranged randomly to give a flower-like open micro-structure. It is apparent from the micrograph that the microstructure of the Co(OH)\(_2\) further agglomerates to form large bunches. The FE-SEM micrograph of Co(OH)\(_2\)/CNT NCs (figure 1(b)) at 40 000 magnification clearly shows that flake-like nano-architecture of the Co(OH)\(_2\) is entangled with CNTs. The nano-flake like morphology of the fabricated product and its effective physical association with CNTs can provide a large number of redox-active sites, and can also accelerate the charge transport process. The fabricated samples were further characterized via powder x-ray diffraction (PXRD) technique to analyze the crystal structure, phase purity, grain size, and % crystallinity. The obtained PXRD patterns of the Co(OH)\(_2\) and its nanocomposite with CNTs are depicted in figure 2(a). The PXRD of Co(OH)\(_2\) display six prominent diffractions peaks at 2\(\theta = 19^\circ\), 32\(^\circ\), 38.2\(^\circ\), 50.9\(^\circ\), 58.3\(^\circ\) and 61.6\(^\circ\) that observed due to the diffractions from the (001), (100), (011), (012), (110) and (111) crystal planes of Co(OH)\(_2\), respectively. All the observed diffraction peaks are in good agreement with the hexagonal phased Co(OH)\(_2\) (JCPDS # 074-1057) [27]. The existence of only characteristics peaks and the absence of any additional peaks confirm the phase purity of the synthesized sample [18].

The PXRD of Co(OH)\(_2\)/CNT NCs, along with characteristics peaks of Co(OH)\(_2\), accommodate one additional broad hump at 2\(\theta \approx 25.5^\circ\) that attribute to the (002) diffraction of the carbonaceous materials [28].

Figure 1. The FE-SEM image of (a) Co(OH)\(_2\) and (b) Co(OH)\(_2\)/CNTs.
In equation (7), \( A_{cp} \) expresses the area under the crystalline peaks while \( A_{ap} \) expresses the area under all peaks. The crystallinity of the fabricated product was come to be 68.2%.

The fabricated products were further characterized by the FT-IR technique to analyze the metal-oxygen bond and various surface functional groups. The FT-IR spectrum of Co(OH)\(_2\) and Co(OH)\(_2\)/CNT NCs, recorded from 350–4000 cm\(^{-1}\), is depicted in figure 2(c). The Co(OH)\(_2\) displays two strong bands at 517 and 615 cm\(^{-1}\) that assign to the stretching and bending modes of Co–O (M–O), Co–O–Co (M–O–M), and O–Co–O (O–M–O) bonds, respectively [30–32]. The –OH group of the Co(OH)\(_2\), because of its starching vibrations, gives a strong and wider absorption band (encircled by a green-line) around 3500 cm\(^{-1}\) [33]. Moreover, two additional bands are observed at 1375 and 1468 cm\(^{-1}\) that can be ascribed to the vibration associated with the carbonate ion (CO\(_{3}^{2-}\)). The CO\(_{3}^{2-}\) ion may be formed on the absorption of atmospheric carbon dioxide [34]. The FT-IR spectrum of Co(OH)\(_2\)/CNT NCs accommodates an extra absorption band at 1598 cm\(^{-1}\) that attribute to the C=C stretching mode in the aromatic rings of CNTs [35].

![Figure 2.](image-url)
Thermal stability, chemical composition, and phase analysis of the fabricated solid-product were completed via thermo-gravimetric technique. The thermo-grams of the Co(OH)$_2$ and its nanocomposite with CNTs are depicted in figure 3.

As apparent from the thermo-graphs, the Co(OH)$_2$ drops its weight in two-steps while Co(OH)$_2$/CNTs NCs drop its weight in three-steps. The weight-drop in the I (up to 190 °C) and II steps (up to 405 °C) is ascribed to the removal of water via adsorption and decomposition processes, respectively [36–38]. The Co(OH)$_2$/CNTs NCs also show an additional weight-drop in additional III steps (up to 556 °C) is ascribed to the burning of carbon-contents (present in the CNTs) [39]. The weight-drop in the III step is almost 4.8% that is much close to the actual % composition (5%) of the CNTs in the fabricated nanocomposite.

The effect of 5% CNTs on the electrical-conductivity of the prepared nanocomposite was also investigated via I–V experiments. Figure 4 displays the I–V profiles of Co(OH)$_2$ and its nanocomposites with CNTs in a voltage range from $-5$ V to $+5$ V.

Apparently, an inverted S-shaped current-voltage profile for the Co(OH)$_2$ (figure 4(a)) indicates its semiconductive behavior. In contrast, almost the liner I–V profile of Co(OH)$_2$/CNTs NCs (figure 4(b)) express its ohmic-response to the applied voltage. The electronic-conductivity ($\sigma$) of the prepared solid-materials was also determined by using their corresponding I–V data in equation (8) [40].
The value of resistance ($R$) was obtained from the inverse-slop of the $I$–$V$ profile, while width ($w$) and area ($A$) of the sample-pellets were determined directly via digital vernier-caliper. The calculated electrical-conductivity values of the Co(OH)$_2$ and its nanocomposite with CNT (Co(OH)$_2$/CNTs NCs) were $8.6 \times 10^{-3}$ Sm$^{-1}$ and $3.2 \times 10^5$ Sm$^{-1}$, respectively. The enhanced electrical-conductivity of the nanocomposite is ascribed to the presence of a highly conductive CNTs.

### 3.2. Superapacitive application

The electrochemical activity of the samples-electrodes was explored by conducting cyclic-voltammetry (CV) experiments in a half-cell configuration.

The CV experiments were completed in a positive potential window that extends from 0 V to 0.6 V. Figure 5 illustrates the comparative CV profiles of the Co(OH)$_2$ and its nanocomposite with the CNTs at the sweep rate of 5, 10, 20, 40, 60, and 80 mVs$^{-1}$.

The CV profiles of Co(OH)$_2$ electrode (figure 5(a)) are non-rectangular and exhibit a pair of oxidation-reduction peaks that suggest the presence of pure pseudocapacitive-mechanism to store charge. The CV profiles of Co(OH)$_2$/CNTs NCs (figure 5(b)) are quasi-rectangular shaped and also exhibit a pair of oxidation-reduction peaks that indicate the contribution of both, non-faradic (EDLC) and faradic mechanism (pseudocapacitance) toward the total capacitance. The oxidation-reduction peaks were observed due to the following reversible transformation [13, 41].

$$\begin{align*}
\text{Co(OH)}_2 + \text{OH}^- + \text{H}_2\text{O} &\leftrightarrow \text{H}_2\text{O} + \text{CoOOH} + e^- \\
\text{CoOOH} + \text{OH}^- &\leftrightarrow \text{H}_2\text{O} + \text{CoOOH} + e^- 
\end{align*}$$

Moreover, the CV profiles of Co(OH)$_2$/CNTs electrode enclose the larger area and exhibit negligible tilt (at extreme potential) than that of Co(OH)$_2$ electrode CV profiles, which indicates the superior capacitive-performance and lower resistivity of the nanocomposite [42]. The improved electrochemical activity of the
nanocomposite based electrode ascribed to the synergistic effects between the 2D nanolakes of Co(OH)$_2$ and 1D CNTs. In fact, Co(OH)$_2$/CNTs NCs because of its two different capacitive supplements, and higher electrical conductivity display outstanding performance. Furthermore, the symmetrically shaped CV profiles of Co(OH)$_2$/CNTs NCs, indicate the electrochemical reversibility of the redox reaction between nanocomposite and electrolyte [18]. In the case of both samples-electrodes, the oxidation-reduction (redox) peaks shifted toward the extreme potentials on increasing the scan rate from 5 to 80 mVs$^{-1}$. This shifting is ascribed to dissimilarity in the migration/transportation rate of the electro-active species at higher scan rates [43].

To get detailed information about the charge-storage mechanism, the relation between the peaks current and scan rate was assumed according to the following power’s law.

$$i = av^b$$  \hspace{1cm} (11)

In equation (11), $a$ and $b$ are variables. The value of $b$ provides valuable information about the type of charge-storage mechanism. When the value of $b = 0.5$ then the charge-storage process is diffusion-controlled while it is capacitive when the value of $b = 1$. Figure 5(c) displays that the $b$ values for Co(OH)$_2$ and Co(OH)$_2$/CNTs are 0.93 and 0.96, respectively [44]. As both samples electrode involve the capacitor-like charge-storage mechanism, hence there specific capacitance (Cs) was calculated via using equation (5).

The influence of the applied sweep rate on the Cs of the fabricated-sample electrodes is depicted in figure 5(d). Evidently, both electrodes exhibit higher Cs at a lower sweep rate while their Cs gradually fades as the sweep rate is increased from 5 to 80 mVs$^{-1}$. In fact, at a lower sweep rate, the maximum interaction between the electro-active species at the interface results in higher capacitance. Moreover, at a lower sweep rate, intercalation pseudocapacitance also contributes toward the total capacitance. This is because at lower sweep rate the electrolyte ions find enough-time and they diffuse into the subsurface (few nm below the surface) of the electrode to develop intercalation pseudocapacitance. In contrast, at a higher sweep rate, the deeper diffusion of the electrolyte ions into the subsurface of the electrode is not possible, hence intercalation pseudocapacitance fails to contribute toward the total capacitance [45].

The cyclic-stability and % capacitance retention of the fabricated electrode-material was also tested against 5000 cyclic (at 70 mVs$^{-1}$). As apparent from figure 6(a), the area under the CV profile of the Co(OH)$_2$ after 5000 cycles considerably decrease that indicated its poor cyclic stability. In contrast, the CV profile of the Co(OH)$_2$/CNTs NCs (figure 6(b)) after 5000 cycles show a negligible area loss that indicates its superior cyclic stability. Actually, 1D CNTs intercalated with the 2D nanosheets of Co(OH)$_2$ and save them against stacking and expansion.

The steady behavior of the electrochemical cell after 5000 cycles (figure 6(b)) can be ascribe to the fact that surface limited redox reaction ($b = 1$) are fast and highly reversible. In comparison, the diffusion limited-redox reaction ($b = 0.5$), that also involve the bulk of the electrode material, result in structural deformation and show less steady behavior on electrochemical tests. In the case of nanocomposite the value of $b$ come to be 0.96 (figure 5(c)), indicating the surface limited redox reaction as a dominant one for charge storage purpose [46].

Figure 6(c) displays a relation between the % capacitance retention and the number of cycles. The % capacitance retention of the Co(OH)$_2$ based electrode decrease as the number of CV cycles increase. After 5000 CV cycles, Co(OH)$_2$ based electrode retains just 71.7% of its initial capacitance. On the other hand, the capacitance retention of the nanocomposite increases up to 102.5% for initial 1500 cycles as the interaction between the CNTs and electrolyte become more efficient with time (activation of the electrode) [47, 48]. After initial 1500 CV cycles, the specific capacitance of Co(OH)$_2$/CNTs NCs also start fading, yet nanocomposite retains 96.2% of its initial capacitance after 5000 cyclic tests.

Specific capacitance, rate-capability, and volumetric efficiency of the samples-electrode were tested via cyclic charge-discharge (CCD) experiments. Figures 7(a), (b) displays the CCD profiles of the Co(OH)$_2$ and its nanocomposite with CNTs at the current density of 0.5, 1, 2, 3, and 5 Ag$^{-1}$. The CCD profiles of Co(OH)$_2$ (figure 7(a)) display prominent discharge-plateaus that have good accordance with the reduction bumbs of their CV profiles. In contrast, the CCD platform of the nanocomposite is distorted triangle-like that ascribed to the contribution of both, EDLCS and PSCs, toward the total capacitance. At the same current densities, the discharge curves of the nanocomposite electrode (figure 7(b)) are more extended than that of Co(OH)$_2$ discharge curves. Much extended discharge curves of the nanocomposite reveal its greater charge-storage capability than that of Co(OH)$_2$.

The Csp of the Co(OH)$_2$ and its nanocomposite with CNT were calculated by using equation (4). The nanocomposite based electrode show superior Csp than that of Co(OH)$_2$ based electrode at all current densities as shown in table 2.

A graph was plotted by using the Csp and current density data of the fabricated samples from table 1 to determine the rate-capability. Figure 7(c) shows the variation of Csp with current density.

The nanocomposite shows superior rate-capability as it preserves 86% of its capacitance at 0.5 Ag$^{-1}$ even at the higher current density of 5 Ag$^{-1}$. Evidently, the Csp of both electrode-materials decreases regularly on
increasing the current density. In fact, at higher current density, the only limited surface area of the electro-active electrode material take-part in faradic reaction while the bulk of the electrode fails to contribute toward the total $C_{sp}$\(^{49}\). The comparison of the closely related but already reported work with the work is given in table 3.

The kinetics of the electrochemical reaction, taking place at the surface or subsurface of the fabricated electrode samples, was examined by EIS spectra analysis. The EIS data of both fabricated samples was employed to draw their Nyquist plots as displayed in figure 8. Evidently, the Nyquist profiles of Co(OH)$_2$ and Co(OH)$_2$/CNTs exhibit a clear semi-circle and a straight-line almost parallel to the $y$-axis. The intersection of the Nyquist curves (at a higher frequency) on the real axis ($x$-axis) indicates the value of solution resistance ($R_{ESR}$\(^{54}\)). As EIS measurements of both samples electrodes were completed in the same electrolyte (3 M KOH) of the same concentration, hence their solution resistance value comes to be the same (3.5 $\Omega$). The semicircle part of the Nyquist curve (at intermediate frequency) semicircle signifies to the charge transfer resistance ($R_{ct}$). To calculate the exact value of the $R_{ct}$ for both sample electrodes, their EIS data were fitted with an equivalent circuit via EC-lab.

The modified Randle circuit, which fitted with EIS data of the nanocomposite electrode, is shown in the inset of figure 8. The $R_{ct}$ value was 8.2 $\Omega$ and 14.4 $\Omega$ for the nanocomposite and Co(OH)$_2$, respectively. Moreover, the slope of the straight line (almost diagonal in position) signifies to the Warburg diffusion resistance ($Zw$) of electrodes. In the case of nanocomposite electrodes, the straight-line part (at low frequency) of the Nyquist plot has larger slop that indicates its lower ion diffusive resistance of the composites\(^{55}\). In fact, the presence of CNTs with superior electrical conductivity in nanocomposite electrode, and good interfacial contact between the Co(OH)$_2$ nanosheets and CNTs produced such ideal impedance characteristics.

The excellent rate capability and good specific capacitance of the Co(OH)$_2$/CNTs was the result of a few key features. Firstly, the CNTs matric enhance the electrical conductivity of the nanocomposite that results in fast-kinetics of the redox reaction. Secondly, a highly conductive redox product (CoOOH) further increases the conductivity of the whole electrode. Thirdly, 2D nanosheets of Co(OH)$_2$ increase the electrode-electrolyte interaction and increase the chance of redox reaction to deliver higher capacitance. Fourthly, CNTs because of their electrical conductivity and higher aspect ratio not only improve the electrical conductive behavior of the
Figure 7. CCD profiles of (a) Co(OH)$_2$, (b) Co(OH)$_2$/CNTs and (c) variation of $C_{sp}$ with current density.

Table 2. The specific capacitance of the Co(OH)$_2$ and its NCs at different current densities.

| Current density (Ag$^{-1}$) | $C_{sp}$ of Co(OH)$_2$ (Fg$^{-1}$) | $C_{sp}$ of Co(OH)$_2$/CNTs (Fg$^{-1}$) |
|----------------------------|-----------------------------------|----------------------------------------|
| 0.5                        | 504                               | 802                                    |
| 1                          | 416                               | 766                                    |
| 2                          | 312                               | 737                                    |
| 3                          | 275                               | 717                                    |
| 5                          | 208                               | 691                                    |

Table 3. The specific capacitance and capacitance retention of the reported Co(OH)$_2$ based electrode and their comparison with current work.

| Materials                | $C_{sp}$ (Fg$^{-1}$)/current density (Ag$^{-1}$) | Ca retention (%)/current density (Ag$^{-1}$) | Ca retention (%)/No. of cycles | References |
|--------------------------|-------------------------------------------------|---------------------------------------------|---------------------------------|------------|
| MWCNT/Co(OH)$_2$         | 570/1.5                                         | 61.9/5                                      | 87.3/5000                       | [50]       |
| Co(OH)$_2$/GNS           | 694/2                                           | 86.4/8                                      | 91.9/3000                       | [20]       |
| Co(OH)$_2$/r-GO NH       | 567/1                                           | 45/8                                        | 82/2000                         | [51]       |
| 3D NrGO/Co(OH)$_2$       | 847/2                                           | 72/10                                       | 95/2000                         | [36]       |
| Flower-like Co(OH)$_2$   | 429/1                                           | 86/5                                        | 80/4000                         | [52]       |
| Whisker-like Co(OH)$_2$  | 325/1.3                                         | 85.8/5.3                                    | 91/1000                         | [53]       |
| rGO/Co(OH)$_2$           | 474/1                                           | 63/10                                       | 90/1000                         | [1]        |
| Co(OH)$_2$/CNTs          | 802/0.5                                         | 91.8/5                                      | 96.2/5000                       | This work  |
nanocomposite but also save it from volume expansions during cyclic tests [56]. Finally, the intercalated OH$^{-}$ ions of the electrolyte help to upgrade the rate capabilities by increasing the interlayer spacing and conductivity.

The electrochemical reversibility and chemical stability of Co(OH)$_2$/CNTs nanocomposite was also checked by conducting EIS and XRD after the cyclic tests. Figure 8(b) display the EIS plots of the Co(OH)$_2$/CNTs nanocomposite before and after 5000 cyclic tests. The $R_{ESR}$ and $Z_w$ of the nanocomposite sample show a very small enhancement after the cyclic tests, indicating the excellent electrochemical reversibility of the redox reaction at the surface of the of the electroactive material. In fact, the $R_{ESR}$ is the sum of contact resistance between the electrode material and electrolyte, ionic resistance of electrolyte, and intrinsic resistance of the electrode material therefore any small change in any one of three constituent change the value of the $R_{ESR}$. The small increase in the value of Zw can be attributing to some structural disorder or volume expansion after 5000 cyclic tests [57]. Furthermore, the phase and structural stability of the Co(OH)$_2$ and Co(OH)$_2$/CNTs against the tedious cyclic tests was also determined via PXRD characterization of their electroactive materials after the cyclic tests. After cyclic tests, the PXRD peaks of the pristine Co(OH)$_2$ sample gets less intense that can be assign to the reduction in crystallinity as a result of volume expansion during the continuous charge/discharge test. Moreover, two additional peaks are also detected that may be arise from the irrepressible product formed as a result of redox reaction. In comparison, the PXRD pattern of the Co(OH)$_2$/CNTs nanocomposite show negligible change before (figure 2(a)) and after (inset of figure 8(b)) the cyclic tests, indicating the retention of the phase and structure of the material after electrochemical test [58].

4. Conclusion

In short, the nanoflakes of Co(OH)$_2$ were synthesized via co-precipitation method while their nanocomposite with CNTs (5%) was prepared by the ultra-sonication approach. The prepared samples were characterized by strong physical techniques such as PXRD, FT-IR, FE-SEM, and I–V. For application studies, the supercapacitive activity of the as-prepared materials electrode was tested in a three-electrode setup via CV and CCD experiments. The result showed that fabricated nanocomposite is potential electrode material for supercapacitor application due to its good specific capacitance (802 F g$^{-1}$ at 0.5 A g$^{-1}$), outstanding cyclic stability, and higher rate-capability. The good specific capacitance of the nanocomposite is the result of synergistic effects between the CNTs and layered Co(OH)$_2$. While the exceptional cyclic-activity and rate-capability is the result of the improved structural and conductive feature of the fabricated composite after CNTs addition. Our fabricated hetero-dimensional nanocomposite (2D layered Co(OH)$_2$ and 1D CNTs) is more efficient for electrochemical applications as its 1D CNTs hinder the stacking of 2D layers of Co(OH)$_2$.

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ORCID iDs

Imran Shakir  https://orcid.org/0000-0002-1843-5139
Zeyad Almutairi  https://orcid.org/0000-0002-1977-8539

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