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Novel fabrication of a nanostructured NiCo$_2$S$_4$/Ni/Ni$_9$S$_8$ composite for energy storage applications

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Abstract

Superior electrochemical behavior for nickel-cobalt sulfide electrodes must be researched and improved. For the storage of energy in supercapacitors, this work, the NiCo$_2$S$_4$/Ni/Ni$_9$S$_8$ nanostructure composite (NCS/N/NS) was created using a solvothermal technique using PEI as a carbon source, followed by argon atmosphere annealing at 500 °C for an hour, followed by a hydrothermal method using thiourea as a sulfur and nitrogen source. NCS/N/NS supplies exceptional electrochemical energy storage features. When used for SCs, the manufactured electrode material, NCS/N/NS, revealed at 1 Ag$^{-1}$ a superb capacitance of 1620 Fg$^{-1}$ (696 Cg$^{-1}$). An NCS/N/NS//activated carbon (AC) asymmetric device was created for practical use by utilizing an NCS/N/NS as the positively charged electrode and the opposite electrode of commercial AC. The asymmetric device achieved a unique specific energy of 53 Wh kg$^{-1}$, with a specific power of 887 W kg$^{-1}$ at 1 Ag$^{-1}$. 
Furthermore, it displays after 3000 cycles, a 100% coulombic effectiveness and a 95% capacity retention, respectively.

**Keywords:** NiCo$_2$S$_4$/Ni/Ni$_9$S$_8$ composites; Nanostructured materials; Battery-type materials; Supercapacitor; Asymmetric device.

**Introduction**

We currently face the pressing issues of environmental degradation and the energy conundrum, which are getting worse as the economy grows. Creating an extremely efficient energy storage device is a crucial step in solving these issues [1, 2]. Supercapacitors (SCs) are an effective energy storage technology that has attracted a lot of attention recently owing to its unique features, which include ultrahigh power density, exceptional electrochemical stability, safety, and environmental friendliness [3-5]. Three distinct categories of electrode materials are employed in SCs: battery-type materials, electric double-layer capacitors (EDLCs), and pseudocapacitive materials. On the basis of the charge storage technique [6]. Using non-Faradaic processes, EDLCs are capable of charging to store in the electrical double-layer interface, which electrostatic adsorption creates among the electrode and the electrolyte. EDLC materials are carbon-based active electrode materials [7]. Pseudocapacitor materials that are reversible Faradaic redox processes are produced close to or at the electrode surface. Specifically, examples include conductive polymers and transition metal compounds [8, 9]. Battery-type supercapacitors employ the Faradaic redox process to store charges through the bulk contact of the electrolyte and electrode at a constant voltage. They use metal oxides [10, 11], metal sulfides [12, 13], and metal hydroxides as their active electrode materials [14]. Among metal species, nickel and cobalt-based compounds have been regarded as viable options
for supercapacitor electrodes due to their excellent electrochemical performance, which includes a high energy density, low cost, and environmentally favorable advantages [15, 16]. Particularly NiCo$_2$O$_4$, owing to its large, generally specific capacitance, eco-friendliness, and reasonable price. But as a result of their low conductivity, specific capacitance gradually decreases due to restrictions on electronic transport [17, 18].

The electrochemical performance might be further enhanced by substituting sulfur for NiCo$_2$O$_4$, which would result in a more flexible structure. This was primarily explained by the fact that oxygen had a higher electronegativity than sulfur [19-21]. Furthermore, it was shown that, compared to NiCo$_2$O$_4$, NiCo$_2$S$_4$ exhibited substantially higher conductivity and a smaller optical band gap energy. So, NiCo$_2$S$_4$ is thought to be an excellent candidate for supercapacitors [22]. NiCo$_2$S$_4$ has several nanostructures, such as flaky arrays [23], nanosheets [24], urchin-like [25], nanocages [26], and mesoporous structures [27]. Li et al. manufactured a carbon@NiCo$_2$S$_4$ using an easy in situ hydrothermal method, which displayed at 1 A g$^{-1}$, a significant specific capacitance (Cs) of 1455 F g$^{-1}$ and after 2000 cycles, a good capacity retention of 83% [28]. Huang et al. created Co$_3$S$_4$@NiCo$_2$S$_4$ nanocages via the exchange of ions technique and vulcanization afterward. Co$_3$S$_4$@NiCo$_2$S$_4$ demonstrated an amazing 1202 F g$^{-1}$ exceptional capacitance at 1 A g$^{-1}$ [29]. Shen et al. manufactured hollow NiCo$_2$S$_4$/Co$_9$S$_8$ electrode nanospheres via sulfuration after an easy hydrothermal method. It demonstrated at 1 A g$^{-1}$ a good Cs of 1008 F g$^{-1}$. NiCo$_2$S$_4$/Co$_9$S$_8$/AC device SC at a power density (P$_d$) of 800 W kg$^{-1}$ has an excellent energy density (E$_d$) of 36.7 Wh kg$^{-1}$ [30].

By the one-step solvothermal method, Jiang et al. generated Ni–Co–S$_4$, which has superb Cs of 2215 F g$^{-1}$ at 1 A g$^{-1}$ and a 90.16% capacitor retention rate following 10,000 cycles.
Furthermore, the Ni-Co–S₄//AC asymmetric device achieved a 36.6 Wh kg⁻¹ ($E_d$) at an 8.5 KW kg⁻¹ ($P_d$), and after 10,000 cycles, it had a capacitance retention of 85.06% [31]. Using a simple anion exchange technique, Ren et al. created mesoporous NiCo₂S₄ with a significant surface area that demonstrated at 1 A g⁻¹ a capacity of 249 mAh g⁻¹, an asymmetric device NiCo₂S₄//AC manufactured at a ($P_d$) of 783 W kg⁻¹, the device has an $(E_d)$of 47.9 Wh kg⁻¹ [32].

In this work, we synthesized a (NiCo₂S₄/Ni/Ni₉S₈) nanostructure composite (NCS/N/NS) using a solvothermal technique, after which it was annealed in an argon environment for one hour at 500°C. This process is followed by hydrothermal synthesis with thiourea as the sulfur and nitrogen source to create the excellently characterized NiCo₂S₄/Ni/Ni₉S₈ nanocomposite. At 1 A g⁻¹, the nanocomposite illustrates an exceptional capacitance with a capacity of 696 C g⁻¹ (1620 F g⁻¹). Additionally, an asymmetric NCS/N/NS//AC device was constructed with a commercial activated carbon AC as the (−) electrode and a NiCo₂S₄/Ni/Ni₉S₈ electrode as the (+) electrode. This asymmetric device produced an exceptional 53 Wh kg⁻¹ ($E_d$) at a ($P_d$) of 887 W kg⁻¹ at 1 Ag⁻¹ and demonstrated after 3000 cycles a 95% capacity retention rate with 100% coulombic efficiency. These findings verify the materials' exceptional capacitive behavior for energy storage applications.

**Experimental work**

**Materials:**

Nickel nitrate hexahydrate (Ni(NO₃)₂.6H₂O, 98%), and Cobalt nitrate hexahydrate (Co(NO₃)₂.6H₂O, >98%) were purchased from Alfa Aesar. Urea (NH₂CONH₂, 99%),
ammonium fluoride NH₄F (98%), thiourea SC(NH₂)₂ (99%), absolute ethanol (C₂H₅OH, 99.8%), and potassium hydroxide (KOH, 85%), from Sigma-Aldrich. Polyethyleneimine (PEI branched, Mₘ = 60,000, 50 wt.% aq. solution) was provided by ACROS. Without any more purification, all of the compounds listed above were employed.

Synthesis of NiCo-PEI (NC-PEI):

The NC-PEI was fabricated using a solvothermal method. By dissolving 0.5 mmol of Co(NO₃)₂·6H₂O and 0.5 mmol of Ni(NO₃)₂·6H₂O with 15 mmol of urea in 30 ml of a solution of PEI in absolute ethanol (5:95% wt/vol.), PEI was used as a matrix for the NC-PEI. Following that, 5 mmol of NH₄F was slowly stirred to get a homogeneous brown solution. A 50-ml Teflon-lined autoclave was filled with the solution and raised to 140°C for 12 hours. resulting in a solid disc of NC-PEI.

Synthesis of NiCo₂O₄/NiO (NCO/NO):

The obtained NC-PEI disc was crushed to powder and then annealed under the argon atmosphere for 1 hour at a temperature of 500°C and a heating rate of 5°C/min to obtain black powders of NCO/NO.

Synthesis of NiCo₂S₄/Ni/Ni₉S₈ (NCS/N/NS):

dissolve 10 mmol of thiourea in 30 ml of deionized water, after that, add 0.05 gm of NCO/NO and sonicate for 1 h. The homogenous solution was then transferred into a 50 mL Teflon-lined stainless-steel autoclave and heated to 140 °C for 12 hours. The autoclave was left to cool down to room temperature. After that, ethyl alcohol and deionized water were used to wash the NCS/N/NS product in order to remove residues, and finally at 60 °C, it was dried overnight.
Characterizations:

The (Bruker AXSD8, ADVANCE, Germany) X-ray diffractometer was used to determine the as-prepared samples’ phase purity and crystallographic features within the 2 Theta range of 10–80°. With a field emission scanning electron microscope (FESEM, Quattro S, Thermo Scientific), surface morphologies and structures were examined. The electronic state of every element was also ascertained by using monochromatized AlKα radiation in X-ray photoelectron spectroscopy (XPS, Thermo Scientific).

Electrochemical Measurements:

Three electrodes were used for the electrochemical tests, and the electrolyte used was a room-temperature, aqueous solution (6 M KOH). The manufactured materials served as the working electrodes. Saturated calomel electrode (SCE) and platinum wire were used as the reference and counter electrodes, respectively. The working electrodes were created through drop-casting processing. By employing a well-mixed slurry with 8 mg of active materials, 1 mg of conductive carbon black, 20 µl of Nafion as a binder in an 80:10:10 weight ratio, and 750 µl of ethanol as a solvent, after cleaning, the nickel foam was covered with the homogenous slurry. Following the electrodes were completely coated at 70 °C, they were dried overnight. An electrochemical workstation (Voltalab 40 PGZ 301, Radiometer Analytical, France) was used to conduct the electrochemical assays. The electrochemical tests, which included cyclic voltammetry (CV) measurements at different scan rates from 200 to 5 mV s⁻¹, were carried out in the operational potential range of -0.2 to 0.5 V. At various current densities of 1 to 10 A g⁻¹, galvanostatic charge-discharge (GCD) measurements were carried out, and utilising the associated discharge curve of GCD, Eqs.
(1) and (2) \[33-37\] were used to determine the specific capacitance \(C_s\) (F g\(^{-1}\)) and specific capacity \(C\) (C g\(^{-1}\)).

\[
C_s = \frac{2I}{mV^2} \int V dt \quad [\text{F g}^{-1}]
\]

\[
C = \frac{I dt}{m} \quad [\text{C g}^{-1}]
\]

The variables (I) and (m) represent the applied current (A), mass (g) of the active electrode, (V) and (dt) denote the applied potential window (V), and the discharging time (s), respectively. The integral area of voltage vs. discharge time of the corresponding GCD discharge curve is described as \(\int V dt\).

Electrochemical impedance spectroscopy (EIS) is also used.

In order to make a hybrid device useful, on NF, NCS/N/NS was used as the positive electrode, and activated carbon AC on NF was used as the negative electrode (made using the drop casting technique, just like working electrodes). 6 M KOH and filter paper were employed as the electrolyte and as the separator, respectively (denoted as NCS/N/NS/AC). identical to the three-electrode system, precise measurements were performed after construction. Equation 3 \[6, 7\] was utilised to compute the mass balance \((m^+ / m^-)\) of two opposite electrodes (positive and negative).

\[
\frac{m^+}{m^-} = \frac{Cs^-\Delta V^-}{Cs^+\Delta V^+}
\]
The negative electrode's particular capacitance is indicated by \( C_s^- \), the positive electrode's specific capacity by \( C_s^+ \), and the negative electrode's potential working window is indicated by \( \Delta V^- \).

Equations 4 and 5 \([10, 13]\) were utilised to estimate the specific energy \( (E_d) \) and related specific power \( (P_d) \) of the asymmetrical device.

\[
E_d = \frac{I \int V dt}{3.6m} \quad \text{[Wh kg}^{-1}\text{]} \tag{4}
\]

\[
P_d = \frac{3600E_d}{\Delta t} \quad \text{[W kg}^{-1}\text{]} \tag{5}
\]

Where \((m)\) is the mass of active material, both the positive and negative electrodes \((g)\), \((\Delta t)\) is the discharge time \((s)\), and \(I \int V dt\) is the area under the corresponding discharge profile of the GCD curve.

**Result and discussions**

XRD has been employed to investigate different electrodes' crystal structures. As illustrated in Figure 1a, an amorphous structure is seen in NC-PEI, and following their annealing into NCO/NO, the peaks located at \(\theta\) of 31°, 36.74°, 44.43°, 59.2°, and 64.95° can be well corresponded with the (220), (311), (400), (511) and (440) of the NiCo\(_2\)O\(_4\) phase (JCPDS Card No. 00-020-0781); in the NiO phase (JCPDS Card No. 03-065-2901), the diffraction peaks at 43.1°, 62.4°, and 75.1° are indexed to the crystal planes (200), (220), and (311). Following sulfuration, in the NiCo\(_2\)S\(_4\) phase (JCPDS Card No. 01-073-1704), the located peaks at \(\theta\) of 31.7°, 38.4°, 55.4°, and 62.6° can be attributed to the planes (311), (400), (440), and (620). The peaks at 44.6° and 52° are indexed to the planes (111) and (200) of Ni (JCPDS Card No. 01-070-0989). The peaks at 27°, 37.1°, 43.1°, 50.6°, and 75°
correspond to the (202), (330), (043), (153), and (227) crystal planes of Ni$_9$S$_8$ (JCPDS Card No. 00-022-1193).

Figure 1. XRD patterns of NC-PEI, NCO/CO, and NCS/N/NS.

Figure 2 shows a high-magnification SEM image to evaluate the morphology and nanostructure of the electrodes, demonstrating that in Figure 2a, the synthesis process allows the insertion of NC-PEI into the templet of carbon in the presence of PEI. After annealing of NC-PEI, as shown in Figure 2b, the crumbles of the PEI carbon template and the appearance of nanoparticles of NCO/NO can enhance electrochemical performance by promoting surface area. Figures 2c and d display that following sulfuration with thiourea as a source of sulfur and nitrogen, nanoparticles of NCS/N/NS have a highly porous structure, leading to excellent electrochemical performance.
Identify the elements' chemical states in NCS/N/NS by XPS. Figure 3a displays the Ni 2p region, which has been separated into the spin-orbit doublets of Ni 2p\(3/2\) and Ni 2p\(1/2\) and satellite peaks at 866.8 and 880.1 eV, respectively. One pair of the spin-orbit doublets is attributed at 856.8 and 873.1 eV, respectively, to Ni 2p\(3/2\) and Ni 2p\(1/2\) of Ni\(^{2+}\). The 861.4 and 875 eV peaks were attributed to Ni 2p\(3/2\) and Ni 2p\(1/2\) of Ni\(^{3+}\), indicating the presence of Ni\(^{2+}\) and Ni\(^{3+}\) in NCS/N/NS [29, 38-40]. The Co\(2p\) region, as illustrated in Figure 3b, depicts the Co 2p\(2/3\) and Co 2p\(1/2\) peaks corresponding to Co\(^{3+}\) at 782 and 797.7 eV, respectively, Co\(^{2+}\) is located at 785.9 and 801.9 eV, and its satellite peaks at 788.1 and 806.6 eV, respectively, indicating the coexistence of Co\(^{2+}\) and Co\(^{3+}\) [41, 42]. The spectra of the S2p region are displayed in Figure 3c. The 2p\(3/2\) and 2p\(1/2\) are in agreement with the peaks
at 168.5 and 169.7 eV, respectively [43]. The C1s region in Figure 3d illustrates peaks centered at 284.5, 285.4, and 289 eV; these values correspond to the C–C/C=O bond, the C–S bond, and the carboxylate carbon (O–C=O) bond, respectively [44-47]. The fitted N1s spectrum is depicted in Figure 3e. The peak values for pyridinic (C≡N−C), pyrrolic (C−NH−C), and graphitic N are 398.1, 399.6, and 401 eV, respectively [41]. Figure 3f displays the O 1s spectrum with a peak at 531.8 eV, belonging to the O–C=O bond, and another peak at 533.4 eV, consistent with the C=O bond [48, 49].
Figure 3. XPS spectrum of NCS/N/NS structure: (a) Ni 2p, (b) Co 2p, (c) S 2p, (d) C 1s, (e) N 1s, and (f) O 1s.
**Electrochemical performance**

To study the electrochemical behavior, the electrochemical analyses were carried out utilizing 6 M KOH. The CV curves of the electrodes for PEI, NCO/NO, and NCS/N/NS are shown in Figure 4a at the scan rate of 50 mV s\(^{-1}\) in a potential range of -0.2 – 0.5 V. The obtained results for all composite materials reveal pair redox peaks, which suggest battery-like behavior. This result is because the electrochemical storage process involves faradaic redox processes [50]. In the CV curves, the electrode's integral area (NCS/N/NS) is greater than the electrodes' PEI and NCO/NO. The NCS/N/NS electrode's highly nanostructured surface and readily available rich active sites are the cause of its superior storage behavior and quick redox kinetics. The NCS/N/NS electrode's CV curves are displayed in Figure 4b at various scan rates. As the scan rate rises, it correspondingly raises the current density. The results show that even with rapid scan rates, the NCS/N/NS electrode material exhibited the characteristics of battery-like charge storage by retaining its evident redox pair. Additionally, slight shifts are observed because more surface sites are contributing to the redox peaks with respect to the scan rate. The redox peaks that correspond to reversible redox faradaic reactions involving Ni\(^{2+}/Ni^{3+}\), Co\(^{2+}/Co^{3+}\), and Co\(^{3+}/Co^{4+}\) are demonstrated in chemical reactions [51, 52]:

\[
\begin{align*}
\text{NiCo}_2\text{S}_4 + \text{OH}^- + \text{H}_2\text{O} & \leftrightarrow \text{NiSOH} + 2\text{CoSOH} + 2e^- \quad (6) \\
\text{CoSOH} + \text{OH}^- & \leftrightarrow \text{CoSO} + \text{H}_2\text{O} + e^- \quad (7) \\
\text{Ni}_{9}\text{S}_8 + \text{OH}^- & \leftrightarrow \text{Ni}_{9}\text{S}_8\text{OH} + e^- \quad (8) \\
\text{Ni}_{9}\text{S}_8\text{OH} + \text{OH}^- & \leftrightarrow \text{Ni}_{9}\text{S}_8\text{O} + \text{H}_2\text{O} + e^- \quad (9)
\end{align*}
\]
Comparative GCD profiles for PEI, NCO/NO, and NCS/N/NS electrode materials at 1 A g\(^{-1}\) are shown in Figure 3c. Additionally, the GCD curves display a plateau-like region that suggests a battery type's faradaic phenomena. The NCS/N/NS electrode displays a longer discharge period as predicted than those of PEI and NCO/NO, exhibiting enhanced electrochemical properties. For the NC-PEI, NCO/NiO, and NCS/N/NS at 1 A g\(^{-1}\), the estimated values of the specific capacitance and capacity of the electrodes are 62.7 F g\(^{-1}\) (26.17 C g\(^{-1}\)), 289 F g\(^{-1}\) (133 C g\(^{-1}\)), and 1620 F g\(^{-1}\) (696 C g\(^{-1}\)), respectively. As demonstrated, the capacitance of NCS/N/NS is higher than that of the other electrodes.

Consequently, it is clear that the porous surface area of NCO/NO that results from annealing gives it a larger capacitance than NC-PEI. NCS/N/NS has the highest capacitance among the other materials. Because sulfur is substituted for oxygen during the sulfurization process due to the fact that the oxygen atom is more electronegative than the sulfur atom, this replacement produces a more flexible structure that enhances electrical conductivity and facilitates the movement of electrolyte ions during faradaic processes [53-55].

Figure 3d exhibits the GCD profile of the NCS/N/NS electrode at various current densities between 1 and 10 A g\(^{-1}\), exhibiting voltage plateaus that match well with the peaks seen in the CV curves that confirm the type of Faradaic. The capacitance and capacity values of the NCS/N/NS electrode are shown in Table 1, with the exception of the NCS/N/NS electrode, which showed unique capacitance performance.

Table 1. Capacitance and Capacity of NCS/N/NS various current densities.

<table>
<thead>
<tr>
<th>Current density (A g(^{-1}))</th>
<th>Capacitance (F g(^{-1}))</th>
<th>Capacity (C g(^{-1}))</th>
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EIS is employed within the frequency range of 100 kHz to 100 MHz. The fitting curve, fitted by Zview™ software, is shown in Figure 3e for NC-PEI, NCO/NO, and NCS/N/NS electrodes. For three electrodes, as shown in Table 2, the fitting results. The NC-PEI, NCO/NO, and NCS/N/NS electrodes have ESR values of 1.4, 1.147, and 1.9 Ω at the high-frequency region, respectively. For the NC-PEI, NCO/NiO, and NCS/N/NS electrodes, the corresponding Rct values are 8, 2.1, and 1.9 Ω, providing a lower Rct value for NCS/N/NS than for the other samples, indicating a rapid rate of charge movement that raises capacitance. On the other hand, the electrode's Warburg resistance (WR) values suggest that the rate of ion diffusion is achievable. The constant phase element (CPEr) The NC-PEI and NCO/NO values are lower than those of the NCS/N/NS electrode because of the increased active sites in the NCS/N/NS electrode [56].

Table 2 shows the NC-PEI, NCO/NiO, and NCS/N/NS electrodes' EIS fitting findings. (a capacitance when CPEp equals 1. b The exponent of the constant phase element. c The resistance to diffusion, or Warburg diffusion resistance. d The time constant for diffusion; e A fractional exponent in the range of 0 to 1.

<table>
<thead>
<tr>
<th></th>
<th>1620</th>
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<td>218</td>
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<tr>
<td>10</td>
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<td>182</td>
</tr>
<tr>
<td>The sample</td>
<td>Rs (Ω)</td>
<td>CPEa</td>
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<tr>
<td>-----------</td>
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</tr>
<tr>
<td>NC-PEI</td>
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</tr>
<tr>
<td>NCO/NO</td>
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<td>0.00563</td>
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<tr>
<td>NCS/N/NS</td>
<td>1.9</td>
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</table>
Figure 4 (a) CV curves of NC-PEI, NCO/NO, and NCS/N/NS at a scan rate of 50 mV s\(^{-1}\), (b) CV curves of NCS/N/NS at different scan rates, (c) GCD of NC-PEI, NCO/NO, and NCS/N/NS at current density 1Ag\(^{-1}\), (d) GCD curves of NCS/N/NS at different current densities ranging from 1 to 10 Ag\(^{-1}\), and (e) EIS plots of the NC-PEI, NCO/NO, and NCS/N/NS.

To examine the practical applications of the NCS/N/NS composite structure, an asymmetric NCS/N/NS/AC device was created, with NCS/N/NS serving as the positive electrode and AC as the negative electrode, respectively. We can determine the operational potential of an NCS/N/NS/AC device by summing the potential windows of NCS/N/NS from -0.2 to 0.5 V and AC from -1 to 0 V. Therefore, the range of potentials between 0 and 1.5 V is suitable for examining the device's electrochemical performance. The CV curves between voltages of 1.4 and 1.6 V at 50 mVs\(^{-1}\), as exhibited in Figure 4a, verify that a range of 0 to 1.5 V is the appropriate operating voltage to prevent any oxygen production [33]. The hybrid device's CV curves for the NCS/N/NS//AC are shown in Figure 4b in an electrolyte of 6 M KOH at scan rates ranging from 5 to 200 mV s\(^{-1}\). The hybrid device's redox faradaic process is indicated by distinct redox peaks on the CV curves. The GCD curves of the NCS/N/NS//AC hybrid device at various current densities are shown in Figure 4c, demonstrating the exceptional reversibility of the hybrid device. The voltage plateau provides further support for the hybrid device's battery-like characteristics. The hybrid device's values of capacitance and capacity are displayed in Table 3.

Table 3. Capacitance and Capacity of NCS/N/NS//AC at various current densities.
<table>
<thead>
<tr>
<th>Current density (A g(^{-1}))</th>
<th>Capacitance (F g(^{-1}))</th>
<th>Capacity (C g(^{-1}))</th>
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</table>

EIS measurements are shown in Figure 4d for the NCS/N/NS//AC hybrid device. From the plot, the hybrid device has an ESR value of 3.3 Ω at the high-frequency region. The corresponding Rct value is 7 Ω, and also, at low frequencies, there is a lower vertical line, which indicates that the ions' diffusion rate is fast. As demonstrated in Figure 4e's Ragone plot, the NCS/N/NS//AC offers the greatest density of energy of 53 Wh kg\(^{-1}\) at an energy density of 887 W kg\(^{-1}\), and even at a power density of 8877 W kg\(^{-1}\), the energy density is able to retain up to 22 Wh kg\(^{-1}\). Remarkably, the NCS/N/NS//AC hybrid device displays better electrochemical performance, making it promising for practical supercapacitor applications. As shown in Figure 4f, the hybrid device displayed exceptional stability; its capacitance retention increased to 95% of its initial value through cycling. Its coulombic efficiency, which, after 3,000 cycles, showed a remarkable 100%.
Figure 4. The CV curves at different voltage windows (a), The CV curves at different scan rates (b), The GCD curves at different current densities (c), The EIS spectrum of hybrid device (d), The Ragone plot for the device (e), and The cycling stability (f).
Conclusions

In summary, an NCS/N/NS nanostructure composite was created utilizing a solvothermal method using PEI (as a carbon source), followed by argon atmosphere annealing at 500 °C for an hour, followed by a hydrothermal method using thiourea as a sulfur and nitrogen source. NCS/N/NS supplies exceptional electrochemical energy storage features. When used for SCs, it exhibited at 1 A g⁻¹ a superb capacitance of 1620 F g⁻¹ (696 C g⁻¹). An NCS/N/NS//activated carbon (AC) asymmetric device with a (P_d) of 887 W kg⁻¹ and a 1 A g⁻¹, The asymmetric device has a coulombic performance of 100%, a capacity retention of 95%, and an outstanding (E_d) of 53 Wh kg⁻¹ after 3,000 cycles.

Acknowledgments

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References