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Article

Surfactant-Assisted Binder-Free NiCo₂S₄ with Enhanced Electrochemical Performance in Aqueous Supercapacitor Application

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Abstract: Until now, crystalline NiCo₂S₄ and its composites have demonstrated improve performances in supercapacitor applications, compared to their oxide analogous, due to their relatively higher electrical conductivity, and multifaceted redox reaction. However, amorphous phase materials have recently shown promise in electrochemical energy storage systems. In this work, urea-assisted amorphous NiCo₂S₄ on nickel foam (referred to as aNCS) with high nitrogen atom% content, was obtained via hydrothermal method. In comparison to the crystalline NiCo₂S₄ (referred to as cNCS), aNCS exhibited superior electrochemical performance with specific capacitance of ~3506 F g⁻¹ which is higher than cNCS specific capacitance of ~2185 F g⁻¹ at 2 A g⁻¹. Additionally, aNCS in two-electrode asymmetry supercapacitor exhibited specific capacitance and energy density of ~196 F g⁻¹ and 56 Wh kg⁻¹, respectively.

Keywords: NiCo₂S₄; binder-free; amorphous; crystalline; supercapacitor; asymmetry

1. Introduction

Supercapacitor with characteristics of high-power density, long cycle life, quick charge-discharge cycle, and environmentally benign is considered one of the electrochemical energy storage systems to tackle diminishing fossil fuel as well as its environmental concerns [1,2]. Generally, supercapacitors are categorized into two main groups according to their energy storage mechanism; electrical double layer capacitors (EDLC), which involves non-faradaic reaction where charge adsorption/desorption occur by electrostatic interactions on the surface of electrode, which give high-rate performance and cycle stability and pseudocapacitors which involves charge storage through faradaic redox reactions within the bulk of the electrode [3,4]. Carbonaceous materials (activated carbon, nanotubes, and graphene) with their characteristic low cost, high conductivity, and large specific surface area, are widely used for EDLC, however, they demonstrate relatively low specific capacitance (~200 F g⁻¹) thereby limiting their practical applications [5]. Whereas, transition metal oxides and conductive polymers are materials commonly explored for pseudocapacitors, and delivers relatively much higher capacitance than EDLCs. However, their poor electrical conductivity and framework swelling during cycling leads to low power density and cycle stability [6,7]. Therefore, electrochemical performance of supercapacitors depends strongly on the properties of the electrode materials [8,9]. Hence, development of materials with the ability to utilize the synergistic properties of EDLC and pseudocapacitor, thereof referred to as hybrid supercapacitors, to give higher capacitance with good rate and cycle performances have been explored [10].

To enhance the capacitance performance of materials, heteroatom (B, N, S) doping, has been demonstrated as one of the effective strategies, due to their ability to modify the surface of the materials [5,11,12]. Notably for nitrogen doping, it has been demonstrated that, the presence of pyrrolic and pyridinic nitrogen which serve as faradaic sites for pseudocapacitance and graphitic nitrogen and pyridinic nitrogen oxide which can enhance the electrical conductivity, are essential to enhance the electrochemical performances of carbon-based materials [11–13]. It is demonstrated that

the presence of high content of nitrogen provides larger surface area leading to high specific capacitance with excellent cycle stability [14,15]. Additionally, it has been shown theoretically that, the low electronegativity of sulfur to oxygen, enable the realization of more flexible structure when oxygen is replaced by sulfur in a material [16]. Thus, transition metal sulfides with relatively higher electrical conductivity resulting from their lower band-gap, which are essential for faster electron transport to enhance electrochemical performance, are of much interest in recent times [16–18]. Among transition metal sulfides, Nickel cobalt sulfides (NiCo_2S_4) have received much attention in recent years for diverse applications such as electrochemical water splitting, gas sensors, supercapacitors, and batteries [19,20]. Despite the promises shown by NiCo_2S_4 in supercapacitor application, it suffers from surface oxidation in alkaline electrolytes and unsatisfactory cycle performance which limit its practical application [21]. To mitigate the above-mentioned problems, various approaches (composite with other materials, tuning the morphology, and varying elemental stoichiometry) have been employed to enhance the electrochemical performance of NiCo_2S_4 [22–26].

Conventionally, NiCo_2S_4 powder are obtained and mixed with conductive carbon and low-conductive binder to form slurry, and subsequently coated on a current collector for subsequent electrochemical analysis. The electron transfer between the electrode material and the current collector might be hindered due to the change in electrical conductivity of the electrode induced by the binder, which limit the rate and cycle performance of the electrode [27]. To limit the side effect of binder on the electrochemical performance of electrode, direct growth of material on current collector, which is subsequently used as binder-free electrode for electrochemical analysis in supercapacitor application, has recently received much attention. Kulurumotlakatla et al. obtained hierarchical NiCo_2S_4 grown on nickel foam which is employed as binder-free electrode for supercapacitor application. It demonstrated specific capacity of $\sim 154.13 \text{ mAh g}^{-1}$ at 2 A g^{-1} , high-rate performance and capacity retention of 95.2% at 4 A g^{-1} after 5000 cycles [17]. Yang et al. obtained binder-free 3D structured flaky arrays of NiCo_2S_4 on Ni-foam through anion exchange of NiCo_2O_4 . The electrode exhibited high specific capacitance of 2044 F g^{-1} at 1 A g^{-1} and capacitance retention of 77% after 2000 cycles [28]. Also, Wen et al. obtained binder-free Ni-Co-S with various Ni/Co ratio, deposited on a carbon cloth, where it was demonstrated that, the ratio of Ni/Co ions are essential in controlling the architecture (morphology) of the material. Here, the optimized electrode showed specific capacitance of 640 F g^{-1} with 84% capacitance retention after 10,000 cycles and energy density 33.9 Wh kg^{-1} at power density 839 W kg^{-1} [29]. Xue et al. fabricated a composite of NiCo_2S_4 nanotubes@NiMn-LDH nanosheets core-shell on Ni-foam, which was employed as binder-free electrode for asymmetric supercapacitor. The electrode demonstrated specific capacity of 822.64 C g^{-1} at 50 mA cm^{-2} with 92.7% capacity retention after 5000 cycles and energy density of 53.1 Wh kg^{-1} at power density 370.82 W kg^{-1} [30].

In recent times, obtaining amorphous phase of material has been considered to be an essential approach to enhance the electrochemical performance of electrode material. The amorphous material is considered to possess more lattice defects than its corresponding crystalline phase, which can provide more active sites to facilitate electron transfer, leading to improved electrochemical properties [31,32]. For example, Sun et al. demonstrated that, amorphous FeO_x nanosheets possess larger interatomic distance and a looser packing than its crystalline counterpart, which resulted in enhanced specific capacity of 263.4 mAh g^{-1} at 0.1 A g^{-1} after 100 cycles, as anode electrode for sodium-ion battery [33]. Additionally, Ren et al. demonstrated that amorphous cobalt sulfide, with more defects and absence of grain boundaries, exhibited superior electrochemical properties as anode in lithium-ion battery [34]. Zhou et al. also obtained various phases of selenium nanowire where the amorphous phase exhibited the highest storage capacity of 755 mAh g^{-1} [35].

In this report, the synthesis of amorphous and crystalline phases of NiCo_2S_4 grown on Ni foam were obtained via hydrothermal method, and their electrochemical performance in supercapacitor application, were investigated. In this approach, surfactant (urea) played a vital role in obtaining the desired phases (amorphous and crystalline), as well as introducing nitrogen doping into the material. The introduction of urea will provide nitrogen doping, which is essential to enhance the electrochemical performance of the material. It was demonstrated that, amorphous NiCo_2S_4 with

higher nitrogen content, exhibited superior electrochemical performance than its crystalline phase counterpart.

2. Materials and Methods

2.1. Chemicals

Nickel (II) nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 99.99%, Aldrich), cobalt (II) hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 97% Junsei), urea ($\text{CH}_4\text{N}_2\text{O}$, 98%, Sigma-Aldrich), hexamethylenetetramine (HMTA, $\text{C}_6\text{H}_{12}\text{N}_4$, 99%, Sigma-Aldrich), sodium sulfide nanohydrate ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$, 98%, Sigma-Aldrich), and activated carbon (AC, Sigma-Aldrich) were purchased and used with no further purifications.

2.2. Material Synthesis

NiCo_2S_4 on nickel foam was synthesized by modified synthesis, reported earlier [36]. Typically, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1 mmol), $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (2 mmol), $\text{CH}_4\text{N}_2\text{O}$ (8 mmol), and $\text{C}_6\text{H}_{12}\text{N}_4$ (6 mmol) were added sequentially to 50ml methanol under continuous magnetic stirring for 30 mins. $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ (4 mmol) was then added to the above solution and stirred for another 30 mins. The formed homogeneous mixture was then transferred into a 100 ml Teflon lined stainless steel autoclave. Subsequently, nickel foam (4.5 cm x 1.3cm) was then immersed into the Teflon containing solution, and hydrothermal synthesis was performed for 18 hrs at 180°C . The nickel foam supported material was removed from the cooled Teflon, washed several times with D.I. water and ethanol, and dried overnight at 60°C to obtain the final product, henceforth referred to as aNCS. A controlled material was also synthesized using the above procedure, using HMTA surfactant only (without urea). The final obtained product is henceforth referred to as cNCS. The average loading mass of NCS on nickel foam is 1.2 mg.

2.3. Material Characterization

X-ray diffraction (XRD) was used to identify the structural phase of the material using a laboratory Rigaku Ultima V diffractometer with $\text{Cu K}\alpha$ radiation source. Field-emission scanning electron microscopy (FE-SEM, JOEL-7800F) and high-resolution transmission electron microscopy (HR-TEM, JEM-2100Plus) were used to observed the morphology and elemental distribution in the material. Elemental composition of the sample was characterized using X-ray photoelectron spectroscopy (XPS, Perkin-Elmer PHI 1600 ESCA system).

2.4. Electrochemical Test

The as-synthesized aNCS and cNCS were used as binder-free electrodes for supercapacitor application. The electrochemical properties, such as cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and impedance spectroscopy (EIS) of the electrodes were obtained in three-electrode system (Biologic SP-150 workstation) with 3M KOH as electrolyte. The binder-free electrodes (aNCS and cNCS), Ag/AgCl electrode and platinum wire were used as working, reference and counter electrodes, respectively. The specific capacitance was estimated based on GCD profiles according to the equation;

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

where C represents the specific capacitance (F g^{-1}), I defines the current (A), Δt refers to the discharge time (s), m represents the loading mass of active material (g), and ΔV refers to the potential window (V).

Additionally, two-electrode asymmetric supercapacitor (ASC) system was also assembled and analyzed for aNCS, where activated carbon (AC) was used as the counter electrode in 3M KOH aqueous electrolyte.

3. Results and Discussion

X-ray diffraction (XRD) analysis was employed to ascertain the structural phases of the samples. Figure 1a, shows the XRD patterns of both samples, where both samples show diffraction peaks at $\sim 45^\circ$, 52° and 77° which is assigned to Ni obtained from Ni-foam substrate.

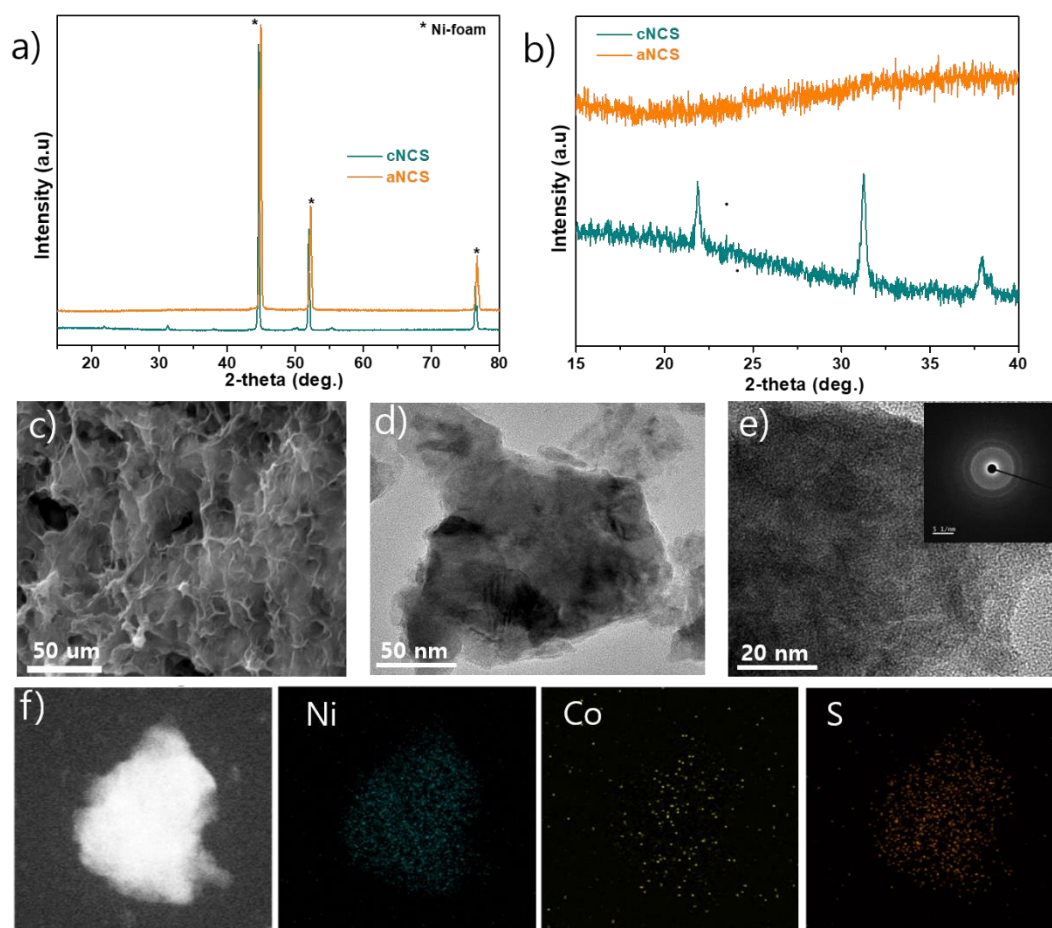


Figure 1. (a) XRD patterns, and (b) Enlarge XRD patterns; of cNCS and aNCS materials compared (c) FESEM image, (d-e) HR-TEM images (insert: SAED pattern), and (g) HAADF-STEM image with corresponding elemental color mapping images; of aNCS.

With further enlargement of the diffraction peaks of both materials (Figure 1b), diffraction peaks were observed for cNCS which matches with NiCo_2S_4 patterns, reported previously [39]. However, for aNCS, there were no diffraction peaks indicating an amorphous state of the sample. The role of urea in the formation of the amorphous phase was confirmed in Figure s1a-b where an amorphous material was obtained when only urea was used as surfactant. This indicates that, introduction of urea during synthesis is essential to obtain amorphous NiCo_2S_4 . The morphology of cNCS (Figure s1c) and aNCS (Figure 1c) demonstrate similar shapes of nanosheet. However, aNCS appears to have smaller nanosheets than cNCS, which can be attributed to the decomposition of urea leading to the release of NH_4^+ and CO_3^{2-} . The release of these gases might have helped form smaller nanosheets, thereby providing larger surface area for higher capacitance. The corresponding TEM image of aNCS (Figure 1d), exhibited the interior structure of the samples which agrees with the SEM images. The HRTEM of aNCS (Figure 1e) and its corresponding SAED pattern (insert: Figure 1e) show a diffused halo ring, which is characteristic of amorphous phase, confirm that, aNCS material is amorphous, which is in agreement with the XRD analysis. However, the SAED pattern of cNCS (insert: Figure s1d) shows a characteristic crystalline phase. The elemental composition of the material was

confirmed by HAADF-STEM color mapping (Figure 1f) of aNCS, which reveal the even distribution of the elements (Ni, Co and S).

Further confirmation of elemental composition and their chemical states were investigated by employing XPS analysis. Figure s2a presents XPS spectrum of both cNCS and aNCS materials, showing the presence of Ni 2p, Co 2p and S 2p. Additionally, it can be confirmed that, both materials contain the same elements as shown in Figure s2b-d. Additionally, the XPS spectra reveals the presence of nitrogen, which can be attributed to the surfactants (HMTA and urea) employed during synthesis. The N 1s spectra of both materials (Figure 2a) show the presence of three peaks at ~398.77-399.2, 402.5 and 406.3 eV which are assigned to pyridinic nitrogen (N-6), graphic nitrogen (N-Q) and pyridine nitrogen oxide (N-O), respectively [5,13,38]. However, aNCS consist of ~5.9 atom % of total nitrogen, which is higher than ~4.49 atom % for cNCS. As shown in Table 1, where aNCS contain higher N-5 and N-O, which are essential to enhance electrical conductivity [39], aNCS material is expected to exhibit superior electrochemical performance than cNCS. This phenomenon confirmed that, the use of urea only not responsible for the amorphous phase formation of NiCo₂S₄ on Ni foam, but also served as N-doping precursor.

Table 1. Summary of N atom content in samples.

Sample	N (atom %)	N-6 (atom %)	N-Q (atom %)	N-O (atom %)
cNCS	4.49	2.70	0.78	1.01
aNCS	5.90	3.22	1.22	1.46

Furthermore, high resolution XPS spectra of individual elements were obtained using Gaussian fitting method (Figure 2b-d). Ni 2p spectrum (Figure 2b) shows two characteristic peaks ascribed to Ni 2p_{3/2} (854.68 eV) and Ni 2p_{1/2} (872.46 eV) together with satellite peaks. Additionally, the devonvoluted spectra demonstrated the co-existence of Ni²⁺ and Ni³⁺ [28]. Similarly, Co 2p spectra (Figure 2c) also show two characteristic peaks assigned to Co 2p_{3/2} (780.23 eV) and Co 2p_{1/2} (795 eV) [40]. In Figure 2d, the S 2p spectra show characteristic peaks at 162.42 eV and 167.83 eV which correspond to S 2p_{3/2} and S 2p_{1/2} respectively [41].

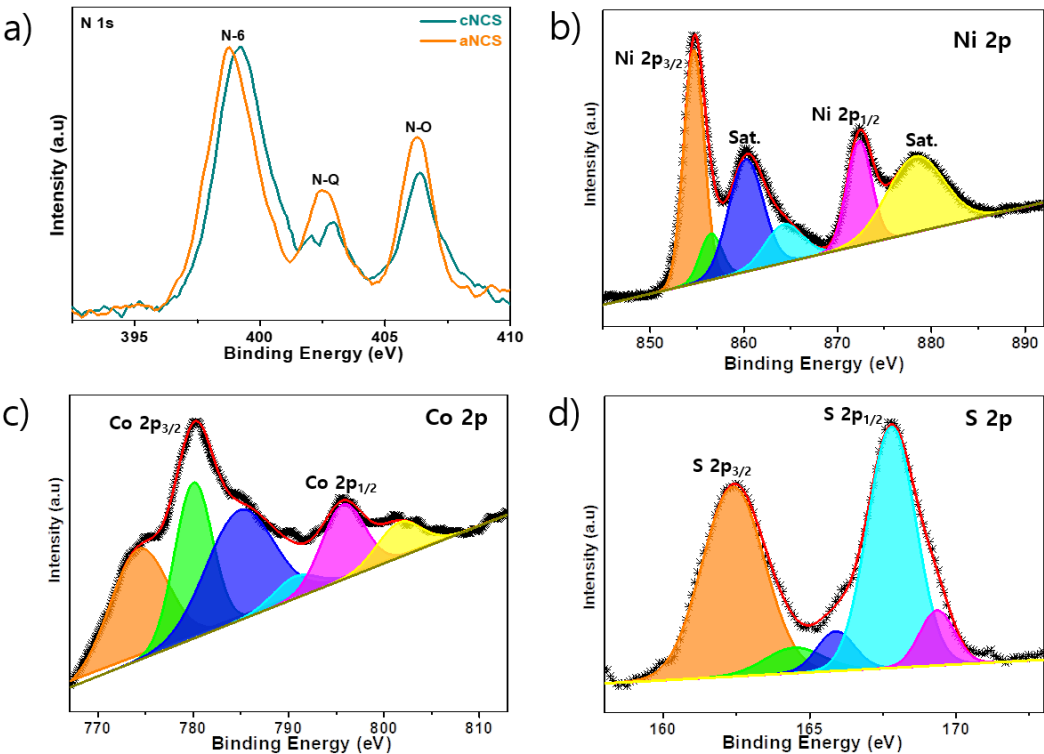


Figure 2. (a) N 1s XPS spectra of cNCS and aNCS samples compared. High resolution XPS peaks of (b) Ni 2p, (c) Co 2p, and (d) S 2p; of aNCS sample.

Additionally, the electrochemical properties of both materials (cNCS and aNCS) were examined in three-electrode system, where the materials with no further treatment were employed as binder-free working electrodes. Figure 3a presents the CV profile comparison of aNCS and cNCS electrode in potential window 0.0-0.5 V at scan rate 10 mV s⁻¹, where both electrodes demonstrate similar distinct curves, which are characteristic of pseudocapacitive mechanism. However, aNCS electrode exhibited larger area, indicating that, it possesses relatively higher storage capacitance than cNCS electrode. Figure 3b and Figure s3a are CV profiles of aNCS and cNCS, respectively at various scan rates (10-50 mV s⁻¹), which show similar redox peaks where the peak current areas increased with increasing scan rates. However, with increasing scan rate, diminishing oxidation redox peaks were observed which can be attributed to inadequate electrochemical reaction time for the electrode active sites [42]. The GCD profiles of the electrodes measured at current density 2 A g⁻¹ are shown in Figure 3c, where aNCS exhibited larger discharge time of 874 seconds compared to cNCS with discharge time of 545 seconds, which implies that, aNCS electrode possesses higher specific capacitance than cNCS electrode. The GCD profiles measured at various current densities (2-10 A g⁻¹) are shown in Figure 3d and Figure s3b for aNCS and cNCS electrodes, respectively, which show excellent electrochemical redox reversibility, demonstrated by their consistent symmetrical profiles with current density. The corresponding rate capability is shown in Figure 3e, where aNCS exhibited superior rate performance with specific capacitance 3506 and 3168 F g⁻¹ compared to 2185 and 1783 F g⁻¹ for cNCS, at current densities 2 and 10 A g⁻¹, respectively. The aNCS electrode also demonstrated superior cycle performance with initial capacitance retention of ~90% compared to ~84% for cNCS, at current density 10 A g⁻¹ after 5000 cycles. The contribution of Ni-foam to the capacitance of the materials were confirmed to be negligible as confirmed by the CV and GCD profiles of Ni-foam, shown in Figure s4. The superior electrochemical performance exhibited by aNCS electrode can be attributed to the higher nitrogen content.

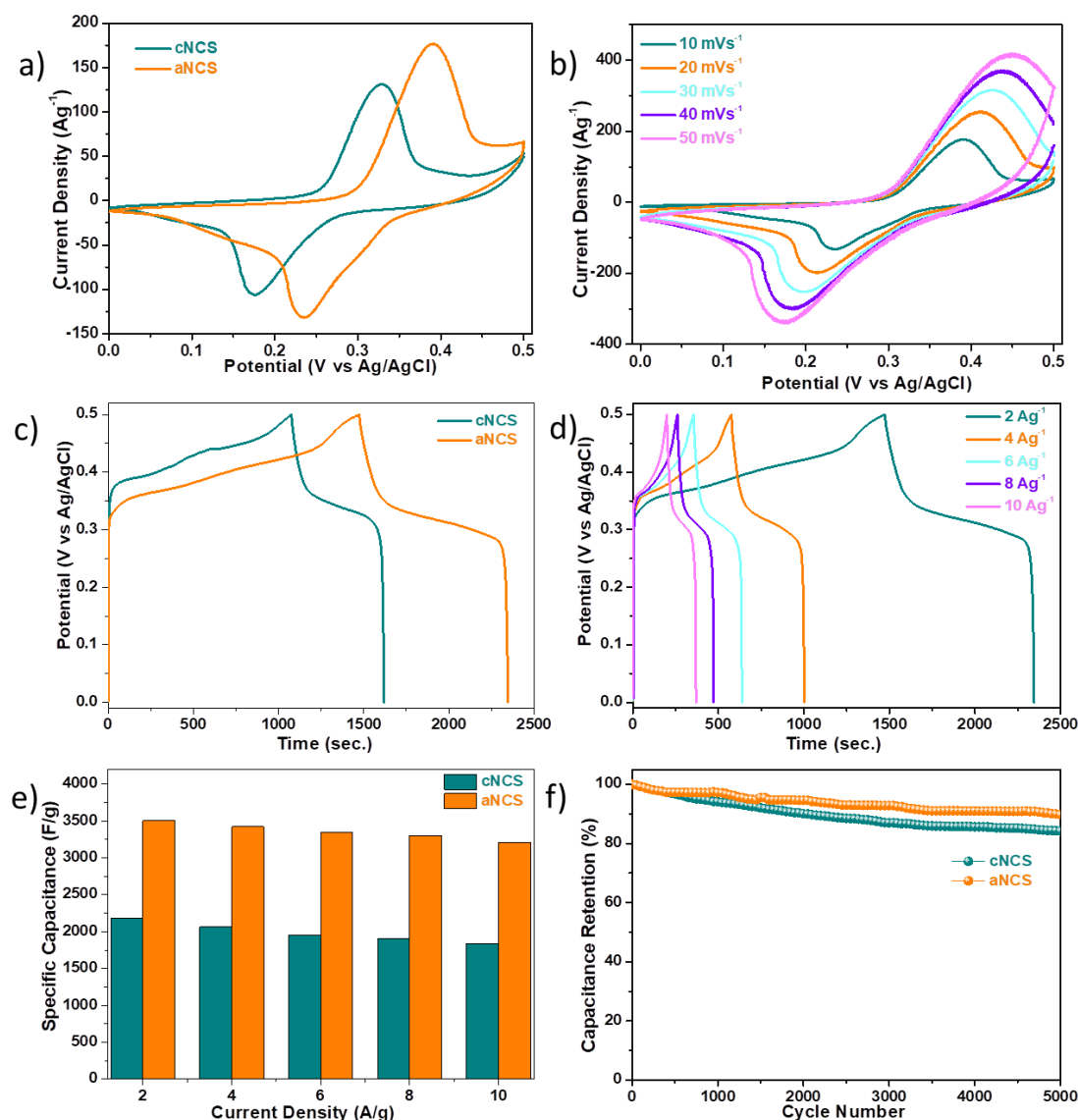


Figure 3. (a) Comparison of CV profiles of electrodes at 10 mV s⁻¹ (b) CV profiles of aNCS measured at various scan rates (c) Comparison of GCD profiles of electrodes at 2 A g⁻¹ (d) GCD profiles of aNCS at various current densities (e) rate capability and (f) capacitance retention of electrodes measured at current density 10 A g⁻¹. All tests were conducted at potential window 0-0.5 V.

This will intend provide larger surface area and enhance the electrical conductivity. This is further confirmed by the lower charge transfer resistance of aNCS than cNCS, as shown in Figure 4a, which implies faster charge transfer in aNCS leading to enhance electrochemical performances [43]. Using the power-law relationship [44], so-called *b*-value was obtained from the CV profiles at various scan rates. From Figure 4b, *b*-values of 0.52 and 0.49 were obtained for aNCS and cNCS, respectively, which demonstrate that the electrochemical reaction of both electrodes is predominantly diffusion controlled. Additionally, by employing the Dunn's method [45,46], we computed the contribution ratio of reaction mechanisms at various scan rates (Figure 4c), where the electrode showed 94% diffusion-driven mechanism at 20 mV s⁻¹(Figure 4d).

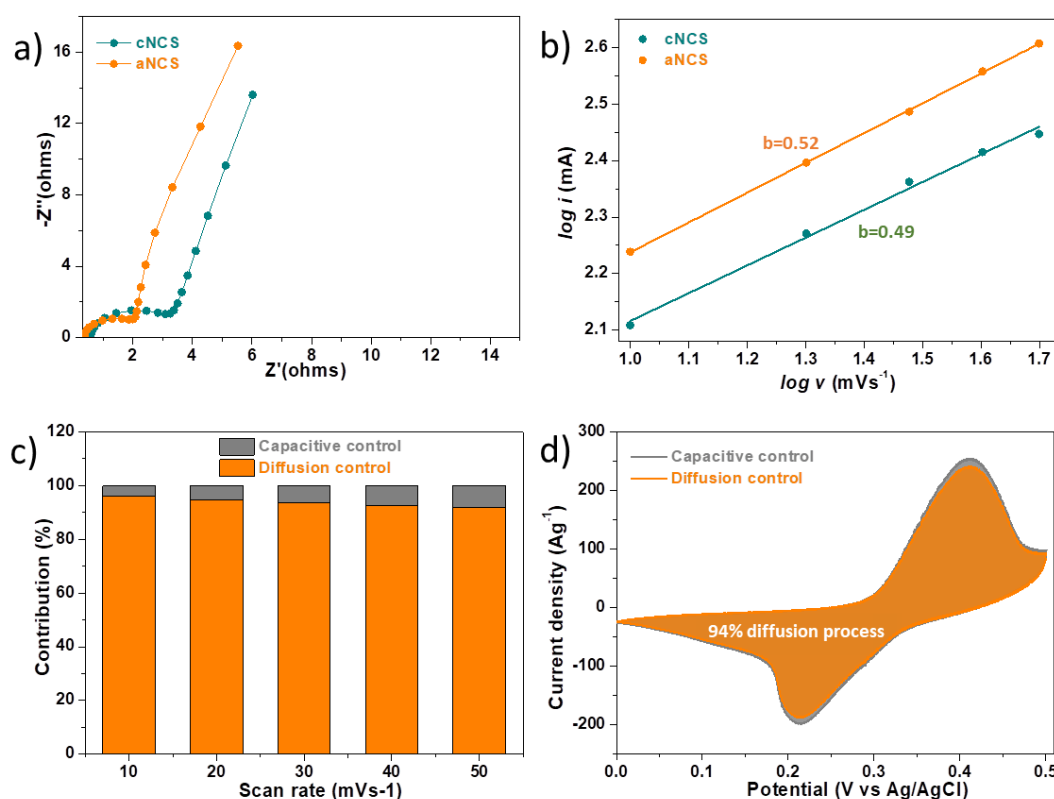


Figure 4. (a) Comparison of EIS plot of the electrodes (b) Plot of $\log v$ against $\log i$, obtained from CV profiles (c) contribution ratio of surface-controlled mechanism to the capacitance of aNCS electrode at different scan rates (f) contribution ratio of surface-controlled mechanism to the capacitance at 20 mV s^{-1} .

For practical application, aNCS electrode was used in a two-electrode asymmetric supercapacitor (ASC) with commercial activated carbon (AC) as counter electrode. Figure s5 presents the CV and GCD profiles of AC obtained using three-electrode system in potential window -1.0-0.0 V in 3M KOH electrolyte. The AC electrode exhibited typical characteristic EDLC behavior with quasi-rectangular and triangular symmetrical shapes by the CV and GCD, respectively. Figure 5a shows the non-overlapping CV profiles of aNCS and AC electrodes at scan rate 10 mV s^{-1} obtained in three-electrode system, to help screen for the stable operating potential window of both electrodes [47].

The CV profiles of the ASC obtained at various scan rates in potential window 0-1.45 V is shown in Figure 5b, where the profiles demonstrated similar shape, suggesting excellent rate performance. The GCD profiles (Figure 5c) and corresponding rate capability (Figure 5d) at various current densities (1-5 A g^{-1}) were obtained, where the electrode demonstrated capacitances 196, 180, 165, 149 and 128 A g^{-1} at current densities 1, 2, 3, 4 and 5 A g^{-1} , respectively. Additionally, the electrode demonstrated excellent initial capacitance retention of ~92.4% at current density 10 A g^{-1} after 5000 cycles. The electrode also exhibited an energy density of 57 Wh kg^{-1} at low power density 960 Wk g^{-1} as shown in Figure 5e. These excellent electrochemical performances exhibited by amorphous NCS were promising in comparison to previously reported work on NiCo_2S_4 and their composites, as shown in Table s1.

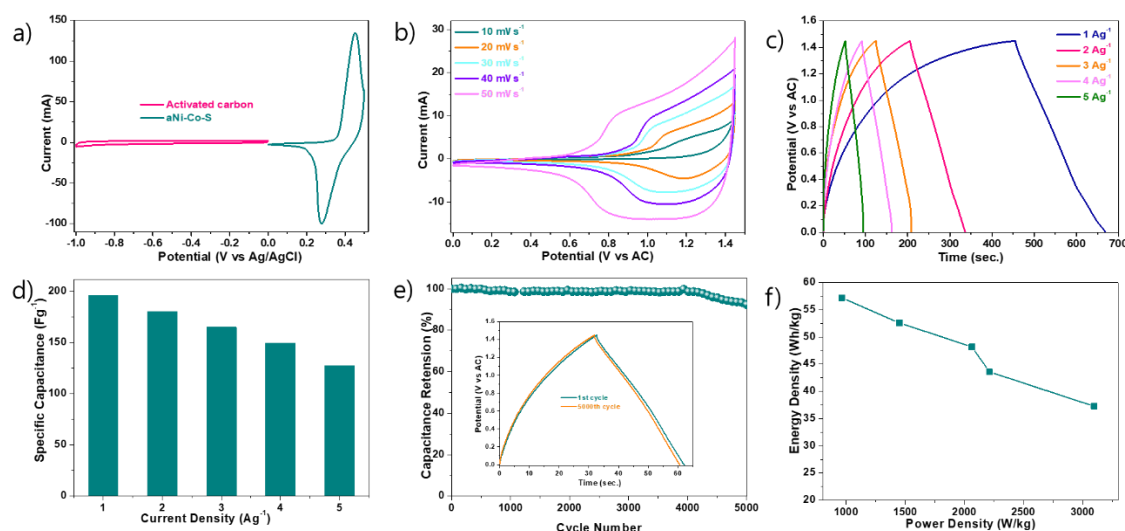


Figure 5. (a) CV profiles of AC and aNCS electrodes measured at potential window -1.0-0.0 V and 0.0-0.5 V, respectively at scan rate 20 mV s⁻¹ in three-electrode system (b) CV profiles at various scan rates (c) GCD profiles at various current densities (d) rate capability (e) capacitance retention (insert: GCD profiles) at current density 10 A g⁻¹ (f) plot of energy density against power density; of aNCS//AC asymmetry supercapacitor measured in potential window 0.0-1.45 V.

5. Conclusions

In summary, crystalline and amorphous NiCo₂S₄ on nickel foam were successfully synthesized, by hydrothermal method. During synthesis, the use urea was vital to successfully obtain the desired phases (amorphous). Additionally, the use of urea also helped increase the nitrogen atom% content in the amorphous material, which is essential to increase the conductivity of the material. When used as binder-free working electrode in three-electrode system with aqueous electrolyte, aNCS demonstrated superior electrochemical performance with higher specific capacitance of 3506 F g⁻¹ compared to 2185 F g⁻¹ for cNCS at current density 2 A g⁻¹. Additionally, aNCS exhibited superior rate capability and cycle performance with 90% initial capacitance retention compared to ~84% capacitance retention for cNCS, after 5000 cycles at 10 A g⁻¹. The superior performance demonstrated by aNCS over cNCS can be attributed to higher nitrogen atom% content caused by the introduction of urea, resulting in superior electron transfer. In two-electrode asymmetry supercapacitor (ASC) system, aNCS electrode demonstrated specific capacitance of 196 F g⁻¹ at current density 1 A g⁻¹. Additionally, the electrode exhibited high energy and power densities of 57 Wh kg⁻¹ and 960 W kg⁻¹, respectively, as well as ~92% initial capacitance retention after 5000 cycles.

Author Contributions: Conceptualization, M.A-A.; methodology, M.A-A.; investigation, M.A-A.; data curation, M.A-A.; writing—original draft preparation, M.A-A.; writing—review and editing, J.I.H.; supervision, J.I.H.; funding acquisition, J.I.H. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: The data presented in this work are available on request from the corresponding author on reasonable request.

Conflicts of Interest: The authors declare no conflicts of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript; or in the decision to publish the results.

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