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Designing nano-heterostructured nickel doped tin sulfide/tin oxide as binder free electrode material for supercapattery

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Abstract

New generation of electrochemical energy storage devices (EESD) such as supercapattery is being intensively studied as it merges the ideal energy density of batteries and optimal power density of supercapacitors in a single device. A multitude of parameters such as the method of electrodes preparation can affect the performance of supercapattery. In this research, nickel doped tin sulfide /tin oxide (SnS@Ni/SnO₂) heterostructures were grown directly on the Ni foam and subjected to different calcination temperatures to study their effect on formation, properties, and electrochemical performance through X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), and electrochemical tests. The optimized SnS@Ni/SnO₂ electrode achieved a maximum specific capacity of 319 C g^{-1} while activated carbon based capacitive electrode exhibited maximum specific capacitance of 381.19 Fg^{-1} . Besides, capacitive electrodes for the supercapattery were optimized by incorporating different conductive materials such as acetylene black (AB), carbon nanotubes (CNT) and graphene (GR). Assembling these optimized electrodes with the aid of charge balancing equation, the assembled supercapattery was able to achieve outstanding maximum energy density and power density of 36.04 Wh kg^{-1} and 12.48 kW kg^{-1} with capacity retention of 91% over 4,000 charge/discharge cycles.

Keywords SnS@Ni/SnO₂, Battery grade electrode, Calcination, Activated carbon, Capacitive, Supercapattery

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Introduction

Electrochemical energy storage devices (EESD) are utilized in almost all consumer electronics and electric vehicles (EVs) in the present world. For instance, in the past decade employment of lithium-ion batteries (LIBs) has seen growing trend in a wide range of industries and sectors to meet the ever-growing energy requirements. Lithium-ion batteries (LIBs) continue to draw vast attention as a promising energy storage technology due to their high energy density, low self-discharge property, nearly zero-memory effect, high open circuit voltage, and long lifespan. However, lithium-ion batteries primarily suffer from low power densities and have tendency to explode or burn upon excessive rise in internal nor external temperatures. This is highly unideal for facilities that require



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mass scale of energy storage as mentioned before to keep electricity demand in check during low energy yield times. On the other hand, supercapacitors are another category of popular devices employed for the purpose of storing energy. Supercapacitors, mainly electric doublelayer capacitors (EDLCs) are known for their fascinating power density and cyclic stability that allows the device to recharge quickly [1-3]. However, it is unable to store large amounts of energy, hindering from becoming the alternative for Li-ion batteries. For instance, Raihan et al. fabricated a solid-state micro-supercapacitor using graphene gel aerosol and reported an exceptional cyclic stability up to 99.6% over 10,000 cycles with a volumetric capacitance of 376.63 mF cm⁻³ [4]. In another work, Zhang et al. prepared a supercapacitor using pecan shell derived ultrathin carbon sheet and reported an excellent power density of 6.35 kW kg⁻¹ with magnifying cyclic stability (95%) over 10,000 charge-discharge cycles [5]. Howbeit, the supercapacitor could achieve the maximum energy density of 15 Wh kg⁻¹.

Therefore, utilizing the concept of hybridization, a new hybrid device known as supercapattery was introduced by merging batteries and supercapacitors. This device is currently being extensively studied as a potential replacement and successor of lithium-ion batteries for industrial scale energy storing capabilities. Supercapattery brilliantly merges the high energy density of batteries and high-power density of supercapacitors to form a hybrid device which is never seen before. The assembly of a supercapattery is performed by using a battery grade electrode and a capacitor grade electrode. The battery grade electrode is specifically used as the positive electrode meanwhile the capacitive electrode is the negative electrode. The battery grade electrode provides the device with optimal energy density. The capacitive electrode enables fast charge storage kinetics compared to the battery grade electrode. In the assembly of the supercapattery, it is crucial to select the suitable electrode materials. Numerous battery grade electrodes have been reported. However, widely applied lithium cobalt oxides have lower capacity and degrade over time further affecting the performance of the battery and are also toxic in nature. Hence, metal sulfides that have relatively better capacity along with less toxicity have been used in this research as battery type electrode material in the assembled supercapattery.

Tin-based chalcogenides namely SnS, SnS_2 , Sn_2S_3 , and SnSe have been extensively explored for its outstanding electrical and optical properties, robust structure, and easy fabrication [2, 6]. Among them, SnS is the most enticing for their physical and chemical properties which can be readily modified to obtain desired electrochemical and optoelectronic performances [7]. Adding on, SnS exhibits a distorted octahedral geometric structure which has large interlayer spacing facilitating the intercalation/ de-intercalation processes during charge storage process [8, 9]. Unfortunately, SnS alone is insufficient to exhibit high specific capacity with energy density in EESDs due to its poor electrical conductivity and structural stability in electrochemical environment, resulting in limited cyclic performance. For example, Ariff et al. synthesized grape-like SnS as the battery grade material for supercapattery and reported a satisfactory energy density of 8.77 Wh kg⁻¹, although it has high specific capacity of 325.20 C g⁻¹ [8]. Addition of metal dopant has shown to enhance the electrochemical performance owing to the changes in the Coulomb field inside the material, creation of synergistic effect between them, and productions of defects to amplify the number of active sites [10, 11]. As an example, Iqbal et al. introduced silver (Ag) as the secondary metal in cobalt sulfide (CoS) and reported that the resulted CoS composite (701.01 C g^{-1}) exhibited specific capacity (289 C g^{-1}) more than two-fold [12]. In another study, nickel-manganese pair was scrutinized and the prepared nickel manganese sulfide//activated carbon (Ni05Mn05S//AC) device exhibited an outstanding energy density of 35.24 Wh kg⁻¹ with specific capacity of 158.6 C g^{-1} [13]. Similarly, tin oxides are widely used in diverse applications namely in energy storage devices (Li-ion batteries and supercapacitors), sensors, and dye-sensitized solar cells for their excellent optical and electrical properties [14, 15]. Individually, these oxides also exhibited high surface area and theoretical capacity and are chemically stable. Thus, to overcome SnS's pitfalls and improvement in electrochemical performance, nickel was specifically chosen as dopant and was incorporated into SnS and concurrently, combined SnO₂ to create enhanced synergistic effect resulted from synergistic of Ni-SnS pair and SnS-SnO₂ heterointerfaces [15–17]. Moreover, the synthesized SnS@Ni/SnO₂ was directly grown on the Ni foam (substrate) to eliminate the unwanted dead weight and internal resistance caused by binder. The SnS@Ni/SnO₂type electrodes were prepared via hydrothermal technique followed by calcination. This work also demonstrates the effect of calcination temperature on the electrochemical performance of SnS@Ni/SnO₂. Apart from optimizing the battery grade material, in this work, a novel approach was adopted to optimize the capacitive electrode by using different combinations of carbonaceous materials. This is where the different weight% (wt%) of conductive material such as acetylene black (AB), carbon nanotubes (CNT) and graphene (GR) in the activated carbon slurry was varied. The well-suited conductive material-active material (activated carbon) pair was used as the capacitive electrode for our SnS@Ni/SnO₂ electrode to investigate the supercapattery performance.

Experimental methods

Materials

Tin(II) chloride (SnCl₂), nickel(II) chloride hexahydrate (NiCl₂·6H₂O), thiourea (CH₄N₂S), acetylene black, graphene (GR), carbon nanotubes (CNT), and poly (vinylidene difluoride) (PVDF) were purchased from Sigma Aldrich, Malaysia. Meanwhile, activated carbon (AC) and N-methyl-2-pyrrolidone (NMP) were purchased at Advanced Chemical Supplier (ASC), Malaysia. Nickel foam (NF) with an exposed area of 1.5 cm \times 1.5 cm was purchased from KGC Resources (M) Sdn. Bhd., Malaysia. Deionized water was used throughout the experiment for synthesis and washing of SnS@Ni/SnO₂ nano-heterostructures.

Synthesis of SnS@Ni/SnO2 electrode

Three precursor solutions and thiourea solution were prepared separately as 30 ml of 6 mM SnCl₂ solution, 20 ml of 2 mM NiCl₂·6H₂O solution, and 10 ml of 24 mM CH₄N₂S solution. 30 ml of SnCl₂ solution was poured into a beaker and placed on a hotplate for stirring at 700 rpm. Both the NiCl₂·6H₂O and CH₄N₂S solutions were then added dropwise using a dropper. The solution was then left to stir at 700 rpm for 30 min. A bare 1.5 cm \times 1.5 cm nickel foam was placed inside the Teflon-lined autoclave. The mixture prepared was then transferred into the Teflon liner and placed in stainless-steel autoclave for hydrothermal process at 150 °C for 6 h. After 6 h, the samples were removed and cooled down. Nickel foam was removed and rinsed with deionized water before being left to dry overnight in the oven at 50 °C. The remnant solution inside the Teflon was then poured into several 15 ml centrifuge tubes for washing. Several washings using deionized water at 6000 rpm for 15 min were done to remove the impurities and excessive precursors. Then, the synthesized SnS@Ni/SnO2 nanostructures were left for drying overnight. To study the effect of calcination temperature towards the synthesized SnS@ Ni/SnO₂, the samples were subjected to different calcination temperatures namely 100 $^\circ$ C, 200 $^\circ$ C, and 300 $^\circ$ C and labelled as SnS@Ni/SnO2-100, SnS@Ni/SnO2-200, and SnS@Ni/SnO₂-300, respectively. For comparison, the sample without calcination temperature was prepared and labelled as SnS@Ni/SnO2.

Preparation of different carbonaceous materials composition as capacitive electrode

AC based slurries were prepared using AC as the main electrode material and the conductive materials such as GR, CNT, and AB were varied to select the optimized conductive material compatible with AC. The binder and solvent used in the slurry preparation were PVDF and NMP. 75:15:10 was the wt% ratio of active material (AC), conductive material (GR/CNT/AB), and binder (PVDF), respectively used to prepare carbon slurry. Firstly, PVDF was added to the NMP solvent and was stirred at 300 rpm at 80°C until the PVDF is fully dissolved. Then, the mixture of AC and AB was added to the solution and left for stirring overnight at 70°C. Similarly, the above steps were repeated for the other carbonaceous materials but, at the final step the AB was replaced with CNT and GR respectively.

Electrochemical performance analysis of SnS@Ni/SnO₂ and AC-based electrodes

Three-electrode setup was used to study the electrochemical performance of all the SnS@Ni/SnO₂ samples. In three-electrode system, SnS@Ni/SnO2 electrode was used as a working electrode, platinum wire as a counter electrode, and silver/ silver chloride solution (Ag/AgCl) as a reference electrode. The setup was immersed in a 1 M potassium hydroxide (KOH) electrolyte solution. Gamry Interface Potentiostat (1010E) was used to conduct Cyclic Voltammetry (CV), Galvanostatic Charge Discharge (GCD) and Electrochemical Impedance Spectroscopy (EIS) analyses. CV was conducted at a potential window of 0 to 0.65 V at scan rates of 5, 10, 20, 30, 40 and 50 mV s⁻¹. GCD was done at current densities ranging from 2 to 10 Ag⁻¹ whereas EIS was conducted in a frequency range of 0.01 Hz to 1 MHz. The electrochemical analyses were conducted on all the electrode samples to select the optimized electrode. For the analysis, average mass loading of SnS@Ni/SnO2 used was 3.0±0.5 mg cm^{-2} .

Similarly, the same setup and analyses were used for the electrodes coated with carbon slurries (capacitive electrodes). Here, the potential window used for CV and GCD tests were -1 to 0 V, and the optimized capacitive electrode based on electrochemical performance was selected for fabrication of supercapattery.

Assembly of supercapattery

Supercapattery was assembled using the best performing electrode sample $SnS@Ni/SnO_2$ as a cathode (battery electrode) whereas an electrode coated with best performing carbon slurry (capacitive electrode) as anode. Electrochemical analyses were then conducted to determine the overall electrochemical performance and the stability of the device. Prior to the assembly of the device, the mass ratio between the electrodes were calculated using Eq. 1:

$$\frac{m_{+}}{m_{-}} = \frac{C_{-}\Delta V_{-}}{Q_{+}}$$
(1)

Where the positive and negative signs in the subscripts of the formula represent the cathode and anode while, C, Q, and ΔV represent the specific capacitance (F g⁻¹),

specific capacity (C g⁻¹) and potential window (V), respectively. The total mass loading of the active material was 4.0 ± 0.5 mg cm⁻² to fabricate a practical supercapattery. According to the previous study, mass loading of a practical device should be >1 mg cm⁻² and lower mass loading leads to overestimation of its electrochemical performance [18].

Results & Discussion

Formation of SnS@Ni/SnO₂

During the hydrothermal process, thiourea undergoes sulfurization releasing sulfur (S²⁻) ions, meanwhile tin salt undergoes hydrolysis releasing Sn²⁺ ions for formation of SnS on the NF. Simultaneously, the hydrolysis of NiCl₂·6H₂O results in the formation of Ni²⁺ and OH⁻ ions, respectively leading to; (i) incorporation of Ni into SnS producing $Ni_3Sn_2S_2$ owing to high activity of Ni [19], and (ii) formation of Sn(OH)₂ with aggregated Sn species that transforms into a stable SnO_2 [20]. It is worth noting that, SnO₂ formation is favourable using hydrothermal method in the presence of hydroxyl ions because of its lower energy barriers and preferred lattice structure [21]. The produced $Ni_3Sn_2S_2$ and SnO_2 nuclei possess high mobility owing to the elevated temperature during hydrothermal process that would give rise to the formation of interconnected nano-heterostructures. The formed nuclei deposit and grow on exposed surface of the NF producing binder-free SnS@Ni/SnO₂.

The influence of calcination at different temperatures on the electrochemical performance of SnS@Ni/SnO₂ electrodes

Characterization of SnS@Ni/SnO2 samples

XRD analysis was performed to confirm the synthesis of $SnS@Ni/SnO_2$ and to determine the crystallinity of the electrode materials. XRD pattern of the samples (Fig. 1(a)) demonstrated major Bragg's reflection peaks at 20 of 26.77°, 32.04°, 34.11°, and 52.02°. Peaks at 26.77°, and 34.11° are attributed to (1 1 0), and (1 0 1) planes of tetragonal SnO_2 phase (JCPDS 02-1340), respectively [22]. Meanwhile, 32.04° and 52.02° are indexed to (0 4 0), and (2 0 2) planes of orthorhombic SnS phase (JCPDS 14–0620) and rhombohedral Ni₃Sn₂S₂ phase (JCPDS 26-1290), respectively [19, 23]. Besides these major peaks, there are also multiple peaks of SnS showing the abundance and dominance of SnS in the active material might be owing to higher concentration of tin precursor and thiourea during the synthesis process.

Notably, XRD patterns of all the samples are similar indicating that calcination could not affect the lattice structure of the $SnS@Ni/SnO_2$ or the chemical composition [24]. The intense peaks within the XRD patterns display good crystallinity nature of the samples [25]. Reduction of intensity with increase in calcination temperature is attributed to the re-arrangement of the SnS and SnS_2 crystal structures when subjected to heat treatment [26]. The formation of $SnS@Ni/SnO_2$ was



Fig. 1 (a) XRD diffractograms of all the prepared SnS@Ni/SnO₂ samples, followed by (b) Rietveld refinement of SnS@Ni/SnO₂

Phase	Atom	Х	Y	Z
SnS	Sn	0.124	0.131	0.250
	S	0.020	-0.630	0.250
$Ni_3Sn_2S_2$	Sn	0.500	0.500	0.500
	S	0.215	0.215	0.215
	Ni	0	0	0.500
SnO ₂	Sn	0	0	0
	0	0.309	0.309	0

further confirmed through Rietveld refinement process using FullProf software and concurrently the changes in parameters affecting the diffraction pattern were investigated (Fig. 1(b)) [27]. The refinement process was done till reduced χ^2 value of 4.97 was obtained. The refined atomic position and structural parameters of SnS@Ni/ SnO₂ are listed in Table 1 and Table 2, respectively.

The surface morphological of the samples deposited on the Ni foam was performed using FESEM and images are displayed in Fig. 2(a-d). All the samples deposited on the Ni foam reveal the are in a uniform surface morphology and heterostructures are interconnected with increased surface area that is available for the electrolyte to penetrate, which in turn accelerates the electrochemical reactions between the electrolyte ions and the active material (SnS@Ni/SnO₂). This leads to an overall excellent specific capacity and rate capability of the SnS@Ni/SnO2 samples [28]. Hierarchical and spherical like nanostructures are perceived in the sample SnS@Ni/SnO2 (Fig. 2(a)) at a magnified scale of 2 µm, meanwhile block like morphology that is gradually increasing in line with the increasing trend of calcination temperature are perceived in Fig. 2(b-d). This suggests that introduction of calcination to the SnS@Ni/SnO₂ has instigated the recrystallization that caused evolution of spherical like nanostructures to

Table 2 Refined cell parameters of SnS@Ni/SnO₂

Phase	Cell Parameters						Space group
	A (Å)	B(Å)	C(Å)	α(Å)	β(Å)	Υ(Å)	
SnS	4.313	11.156	3.969	90	90	90	Pbnm
Ni ₃ Sn ₂ S ₂	5.406	5.406	5.413	90	90	120	R-3 m
SnO ₂	4.728	4.728	3.178	90	90	90	P42/mnm



Fig. 2 FESEM images of (a) SnS@Ni/SnO₂(b) SnS@Ni/SnO₂-100 (c) SnS@Ni/SnO₂-200 (d) SnS@Ni/SnO₂-300 electrodes at magnification 50,000 x, (e) EDX spectroscopy of SnS@Ni/SnO₂ and (f) HRTEM of SnS@Ni/SnO₂

bulky block like microstructure, which supports the XRD results. Although, bulky microstructures are expected to have better crystallinity compared to spherical nanostructures (SnS@Ni/SnO₂), but SnS@Ni/SnO₂ possesses a better surface to volume ratio that exposes more active site for enhanced redox reactions [29]. Apart from that, SnS@Ni/SnO₂ is expected to have a shorter transportation pathway for electrons movement, facilitating the rapid charge transfer kinetics. Since the XRD pattern revealed no significant changes in the chemical composition among the samples, thus the EDX and HRTEM analyses were performed for the optimized sample (SnS@Ni/ SnO_2) only. EDX displayed in Fig. 2(e) corroborated the presence of Sn, S, O, and Ni elements, together revealing uniformly distributed particles with dominant SnS supporting the XRD pattern. HRTEM analysis (Fig. 2(f)) reveals an aggregated spherical-like morphology similar to Fig. 2(a) with an average d-spacing of 0.36 nm that is indexed to the $(1\ 1\ 0)$ plane.

Electrochemical analysis of SnS@Ni/SnO₂ samples

The charge storage mechanism of the samples was investigated using CV. Figure 3(a-d) depicts the CV curves for SnS@Ni/SnO₂ electrode at different calcination temperatures. The CV curves for individual samples display a battery-type pattern that proves the ability of the SnS@Ni/ SnO₂ electrode samples to store the charge. The peak on the other hand serves as evidence for the occurrence of faradaic redox reactions that allows the storing of charge mechanism within the battery type electrodes. When the scan rate is increased, the shape of the CV curve remains consistent, indicating that the SnS@Ni/SnO2 material has good rate capability and reversibility, meaning it can maintain its electrochemical properties under high current density without significant deterioration [30]. The movement of the redox peak to the right in the CV curve with an increasing scan rate is due to the increase in internal resistance of the electrode as more electrons are required. By referring to Fig. 3(e), it is observed that by comparing the different samples at a constant scan rate of 5 mVs⁻¹, SnS@Ni/SnO₂ sample exhibits the largest area of CV curve that indicates the highest specific capacity among the samples [31].

Specific capacity is the measure of the ability of a material to store electrical charges per unit mass. Specific capacity, Q_p can be determined by calculating the area under the CV curve by using the following Eq. 2:

$$Q_p = A/2mk \tag{2}$$

Where A is the integrated area under the curve (cm²), m is the mass of active material deposited (g), and k is the scan rate (mVs⁻¹). By using the Eq. 2, the obtained values for the C_s at 5 mV s⁻¹ of SnS@Ni/SnO₂, SnS@Ni/

 $SnO_2\mathchar`eq Ni/SnO_2\mathchar`eq 200$ and $SnS@Ni/SnO_2\mathchar`eq 300$ are 295.88 C g⁻¹, 305.40 C g⁻¹, 248.95 C g⁻¹, and 144.27 C g⁻¹, whereas the C_s of SnS@Ni/SnO₂, SnS@Ni/SnO₂-100, SnS@Ni/SnO2-200 and SnS@Ni/SnO2-300 at 50 mV s⁻¹ are 44.53 C g⁻¹, 88.58 C g⁻¹, 113.38 C g⁻¹, and 86.92 C g⁻¹, respectively. It is concluded that the SnS@ Ni/SnO2 and SnS@Ni/SnO2-100 exhibit nearly the same C_s at 5 mVs⁻¹, and as the scan rate increases to 50mVs⁻¹, the specific capacity drop is lesser for SnS@Ni/SnO2-100 than SnS@Ni/SnO2 suggesting that calcination has improved the rate capability that might be owing to its improved crystallinity [32]. However, CV comparison curve in Fig. 3(e) discloses that SnS@Ni/SnO₂ exhibits the largest area under the curve leaving a perception that SnS@Ni/SnO2 could have larger charge storage capacity than other samples.

To corroborate the CV results, galvanostatic charge/ discharge (GCD) analysis was conducted for these electrode samples at varying current densities of $2-10 \text{ Ag}^{-1}$. It is worth noting that the potential window in GCD analysis was set to 0 V to 0.5 V to eliminate local overpotential occurrence that could affect the electrochemical performance of the sample (see Fig. 3). This is because appearance of, a "tail" in duck shape from 5 mV s^{-1} till 30 mV s⁻¹ beyond 0.5 V in CV curves, signifying the occurrence of local overpotential [30, 33]. The almost symmetrical shape of the curves indicates that the electrodes possess Faradaic behavior and significant reversibility. The test results show that as the current density increases, the discharge time decreases due to a shorter time for charge carriers' movement at the electrodeelectrolyte interface. Based on Fig. 4(a), SnS@Ni has the longest discharge time at 2 Ag^{-1} , that depicts high energy density, hence longer time is needed to completely undergo complete discharge. The discharge GCD curves were used to calculate specific capacity (Q_s) , energy density (E), power density (P), and rate capability. The formulas for these are given in Eq. 3, and 4:

$$Q_s = (I \times \Delta t) / (m) \tag{3}$$

$$Rate \ capability = Q_s/Q_i \times \ 100\% \tag{4}$$

where Δt is discharging time (s), m is active mass of the material (g), ΔV is potential window (V), and Q_i is the initial specific capacity (C g⁻¹).

As predicted, the calculated specific capacity of SnS@ Ni/SnO₂ (319.00 C g⁻¹) at 2 Ag⁻¹ reveals the highest followed by SnS@Ni/SnO₂-100, SnS@Ni/SnO₂-200, and SnS@Ni/SnO₂-300 of 240.00 C g⁻¹, 198.60 C g⁻¹ and 121.60 C g⁻¹, respectively (Fig. 4). The SnS@ Ni/SnO₂ exhibited a specific capacity of 154 C g⁻¹ at 7 Ag⁻¹, retaining 48% of its rate capability, while SnS@Ni/SnO₂-300 and SnS@Ni/SnO



Fig. 3 Cyclic voltammetry curves at different scan rates of 5 mVs^{-1} to 50 mVs^{-1} for **(a)** SnS@Ni/SnO₂, **(b)** SnS@Ni/SnO₂-100, **(c)** SnS@Ni/SnO₂-200, (d) SnS@Ni/SnO₂-300 and **(e)** comparison of all fabricated electrodes based on SnS@Ni/SnO₂ at a scan rate of 5 mV s^{-1}



Fig. 4 GCD curves at different current densities for (a) SnS@Ni/SnO₂, (b) SnS@Ni/SnO₂-100, (c) SnS@Ni/SnO₂-200, and (d) SnS@Ni/SnO₂-300

had values of 154 C g⁻¹, 137.90 C g⁻¹ and 93.31 C g⁻¹, respectively, retaining 64%, 69%, and 77% of their rate capabilities. It is perceived that calcination has improved the rate capability of the samples due to increase in particle size and crystallinity [32, 34]. This is because of calcination of $SnS@Ni/SnO_2$ at high temperature that provided sufficient energy for the crystal grain growth and caused increase in particle size [34]. Increased in particle size reduces the accessible active site. Therefore, even at higher current density, the electrolyte ions can access most of the active sites resulting in the high-rate capability. However, decrease in accessible active sites

deteriorates the specific capacity owing to the reduced interacting species for faradaic reaction.

In short, it is perceived that $SnS@Ni/SnO_2$ has the largest specific capacity at diverse current density compared to the calcined $SnS@Ni/SnO_2$ samples. This might be owing to the excellent interaction of electrolyte ions with active material. Apart from that, the interconnected spherical nanocomposites would provide a higher exposed active site owing to their higher surface to volume ratio compared to bulky structure which is favorable for charge storage applications. Smaller particle size also

would reduce the transportation time as is proportional to the square of the size of the nanostructure (t α L²) [29].

EIS of fabricated electrodes was performed over a frequency range of 0.01 Hz to 1 MHz. The Nyquist plot of the electrodes is shown in Fig. 5. The equivalent series resistance (ESR) is determined by figuring out the x-intercepts of the plot (see the inset graph of Fig. 5) [35]. The x-intercept values of the 4 samples; SnS@Ni/ SnO₂, SnS@Ni/SnO₂-100, SnS@Ni/SnO₂-200, SnS@ Ni/SnO₂-300 are 0.95 Ω , 0.56 Ω , 0.45 Ω , 1.34 Ω respectively. It is perceived that SnS@Ni/SnO₂-200 has the lowest ESR among all the samples, might be owing to the tightly packed and uniform growth of the SnS@Ni/SnO₂ under 200 °C calcination temperature. Meanwhile, SnS@ Ni/SnO₂-300 possesses the highest ESR because of the overgrowth of SnS@Ni/SnO2 which led to agglomeration of the particles. From the EIS spectra, it is revealed that SnS@Ni/SnO $_2$ exhibits a slightly higher ESR value than SnS@Ni/SnO₂-200, might be owing to the agglomeration of the spherical nanoparticles. In a typical EIS spectrum, a semicircle at a high frequency region is perceived reflecting the charge transfer resistance (R_{ct}) [36]. In all the samples, semicircle is not observed suggesting that the R_{ct} of prepared $SnS@Ni/SnO_2$ is significantly low. Thus, the equivalent series model as disclosed in the inset of Fig. 5 was fitted and R_{ct} values were obtained. The R_{ct} value of $SnS@Ni/SnO_2$, $SnS@Ni/SnO_2$ -100, $SnS@Ni/SnO_2$ -200, $SnS@Ni/SnO_2$ -300 was 0.16 $\mu\Omega$, 0.32 $\mu\Omega$, 0.24 $\mu\Omega$, and 0.17 $\mu\Omega$, respectively. $SnS@Ni/SnO_2$ exhibits the lowest R_{ct} suggesting that it has shortest ion diffusion pathway all over the electrodes [37]. Although, ESR value of $SnS@Ni/SnO_2$ is slightly higher, the lowest R_{ct} value supports the superior electrochemical performance.

Assembly of supercapattery Optimization of capacitive electrode

Three different carbon slurries were prepared with alteration of conductive material using acetylene black, carbon nanotube and graphene designated as samples AB, CNT, and GR respectively. Cyclic voltammetry was conducted to obtain the CV curves of the AC electrode using the three-electrode system. Based on Fig. 6, the CV curves of AB, CNT, and GR based working electrodes were observed to attain a rectangular shape. The rectangular



Fig. 5 Nyquist plot of the fabricated SnS@Ni/SnO2 electrodes



Fig. 6 CV curves of (a) AB, (b) CNT, and (c) GR based capacitive electrodes

shape of CV curves confirms the capacitive nature of the electrodes [38]. The ideal shape retention over high scan rate (50 mV s⁻¹) also suggests that electrochemical stability of the capacitive electrodes is excellent. Since the area of the CV curves indicates the charge storage capacity of the sample. From Fig. 6, it is estimated that AB and GR can store a larger specific capacitance than CNT. The specific capacitance value of CNT is deemed to be very small along with depicting a narrow CV curve

as in Fig. 6(b) due to possible agglomeration and stacking of the tubular CNTs on the nickel foam during the fabrication process [39]. This led to a lower rate of charge carrier movements and reduced mobilities of ions during charge-discharge.

To corroborate the CV results, GCD analysis of the three capacitive electrodes was also done and the resulting discharge curves were plotted as shown in Fig. 7. The GCD analysis was carried out at current density ranging from 2 Ag^{-1} to 10 Ag^{-1} . As expected, it is observed that AB electrode took the longest time of 80 s to discharge completely. This is due to attaining a higher energy density and storing more charge that is ideal for maximizing the energy storage capacity of the capacitive electrodes. Meanwhile, both CNT and GR seem to discharge at a much faster rate due to minimum charge storage capacity as seen in Fig. 7(b) and (c).

The obtained specific capacitances for the 3 samples were calculated from the GCD data. Therein, Cs of AB, CNT and GR are calculated to be 381.19 Fg^{-1} , 258.66 Fg⁻¹ and 36.98 Fg⁻¹, respectively. This depicts that the specific capacitance of AB is the highest where the capacitance of GR is the lowest among all three samples. AB also achieved the highest rate capability of 62% compared to the CNT and GR based capacitive electrodes having 31% and 39%, respectively AB tends to perform better at storing the charge and charge-discharge rate due to higher sp² carbon atoms compared to CNT and GR that has lower proportion of sp²



Fig. 7 GCD curves capacitive electrode of (a) AB, (b) CNT, and (c) GR at current density range of 2 Ag⁻¹ to 10 Ag⁻¹

carbon atoms and higher sp³ carbon atoms. The structural arrangements of sp² carbon atoms are more ideal compared to sp³ carbon atoms as sp² carbon atoms attain more planar hexagonal structure that enable a better electrolyte penetration and enhanced charge carrier conductivity within the electrodes [40]. Apart from that, increase in sp² conjugated carbon atoms leads to the formation of continuous conducting network that delocalizes the electrons of Λ bond for charge transportation [41]. AB is expected to agglomerate and form conducting network for AC to be bonded within the network, meanwhile CNT is expected to form clusters and be dispersed in between the AC. Finally, the 2D GR nanoflakes are expected to homogenize well with AC. According to previous study, it was revealed that combination of AC-GR and AC-CNT exhibited better specific capacitance compared to AC-AB because its higher electrochemical surface area compared to AB [42]. However, in this case, AB exhibited the highest specific capacitance, that might be because of 15 wt% is the optimum ratio mixture for AC-AB pair while modification in the ratio of the CNT and GR is required to achieve the optimum performance of each combination. Figure 8 depicts the Nyquist plots of AB, CNT, and GR based electrodes. The ESR values of the electrodes can be obtained by determining the exact point of x-intercepts on the plotted graph. A magnified section of the plot presents the x-intercept values or ESR values of the AB, CNT, and GR electrodes to be 0.79 Ω , 1.10 Ω and 1.16 Ω respectively. AB electrode attains the lowest value of ESR relative to the other two electrodes that supports the better charge storage capacity as lower resistance is beneficial for better charge storage mechanism. This relates back to a more homogeneous and planar atomic structure of AB that makes it a better carbon material for capacitive electrode applications as the mobility of charge carriers is better and faster [43]. There was no obvious semi-circle observed in the EIS graphs suggesting that addition of the conductive additives has improved the electrical contacts of the AC particles [44]. It also suggests that the R_{ct} value of all the conductive additives is low



Fig. 8 Nyquist plots of capacitive electrodes



Fig. 9 Electrochemical analyses of SnS@Ni/SnO₂/NF//AB/NF: (a) CV (b) GCD (c) Lifecycle analysis over 4,000 charge-discharge cycles with inset of EIS before and after lifecycle

Table 3 Electrochemical performance of SnS@Ni/SnO ₂ /NF//AB/	
NF compared to previously reported binary metal sulfide based	
supercapattery	

Device	Elec- tro- lyte used	Maximum energy density (Wh kg ⁻¹)	Maximum power density (W kg ⁻¹)	Ref.
SnS//AC	1 M KOH	8.77	3,095	[8]
Zn-Sn-S//AC	1 M KOH	30.06	3,200	[45]
AgCoS//AC	1 M KOH	22.34	5,100	[12]
NiMnS-PANI//AC	1 M KOH	35.73	3,500	[46]
SnS@Ni/SnO ₂ /NF//AB/NF	1 M KOH	36.04	12,480	Our work

suggesting an enhanced adsorption/desorption processes at the electrode-electrode interface, delivering a superior electrochemical performance.

Electrochemical performance of optimized battery type and capacitive electrode based supercapattery

Supercapattery was assembled using the optimized battery type and capacitive electrodes which are SnS@ Ni/SnO₂ and AB, respectively. The assembled supercapattery, SnS@Ni/SnO₂/NF//AB/NF was then analyzed electrochemically via CV, GCD and EIS techniques as depicted in Fig. 9. Figure 9(a) illustrates the CV curves of the supercapattery at scan rate of 5 mVs⁻¹ to 50 mVs⁻¹ in a voltage window of 0 to 1.60 V. A distinct CV curves were perceived primarily originated from the nature of battery like material SnS@Ni/SnO₂ and capacitive material of AB (Fig. 9(a)). A retained shape throughout the various scan rates from 5 mV s⁻¹ to 50 mV s⁻¹ however proves the stability of the energy

storage device and the reversibility of both the faradaic and non-faradaic processes. The device achieved a satisfactory specific capacity of 60.19 C g⁻¹ and 41.38 C g⁻¹ at 5 mV s⁻¹ and 50 mV s⁻¹ from CV analysis, respectively.

For GCD analysis, it was perceived that the assembled supercapattery has electrochemical stability over 1.75 V. Thus, to study the device's performance at extended voltage, GCD analysis was carried out in a voltage window of 0 to 1.75 V in the current density range of 2 Ag^{-1} to 10 Ag^{-1} as shown in Fig. 9(b). The discharge time of 96 s at 2 Ag^{-1} was observed that is a promising performance of the device. The curves are also symmetrical that suggests a good charging reversibility for energy storage applications. The calculated specific capacity values of the device at 2 to 10 Ag⁻¹ were 157.08 C g⁻¹, 133.20 C g⁻¹, 116.00 C g⁻¹, 106.70 C g⁻¹, 99.96 C g⁻¹, 93.84 C g⁻¹, 87.15 C g⁻¹, 82.39 C g⁻¹, and 77.34 C g⁻¹, respectively. The specific capacity reduces slightly at higher current density (10 Ag^{-1}) as there was insufficient time for the charge carriers to completely absorb and travel in and out of the electrodes. The rate capability was 62% at 10 Ag^{-1} which suggests a good electrochemical stability of the device.

The maximum energy density and power density of the samples were calculated using Eqs. 5 and 6, respectively.

$$E = (Q_s \times \Delta V) / (2 \times 3.6)$$
(5)

$$P = (E \times 3600) / \Delta t \tag{6}$$

where Δt is discharging time (s), m is active mass of the material (g), ΔV is potential window (V), and Q_s is the specific capacity (C g⁻¹).

The device exhibited an outstanding and competitive maximum energy density of 36.04 Wh kg^{-1} at power density of 3.30 kW kg⁻¹. Besides, the SnS@Ni/ SnO₂/NF//AB/NF could achieve a fascinating maximum power density of 12.48 kW kg⁻¹ retaining energy density of 13.41 Wh kg⁻¹, making the Ni incorporated SnS/SnO₂ paired with the optimized capacitive electrode as the potential combination in energy storage applications. From the performance, it suggests that most of the energy density capability has been contributed by the battery-grade electrode (SnS@Ni/ SnO₂) whereas the high-power density is achieved through the integration of AB capacitive electrode. Compared to energy and power densities of the previously reported supercapatteries' namely SnS//AC (8.77 Wh kg⁻¹ at 806.8 W kg⁻¹) [8], Zn-Sn-S//AC $(30.06 \text{ Wh kg}^{-1} \text{ at power density } 3.20 \text{ kW kg}^{-1})$ [45], AgCoS//AC (22.34 Wh kg⁻¹ at 899.2 W kg⁻¹) [12], and NiMnS-PANI//AC (35.73 Wh kg⁻¹ at 850 W kg^{-1}) [46], our device exhibited a competitive energy density and power density. A comparison of this work with previous metal sulfide-based supercapatteries is presented in Table 3. To determine the cyclic stability of assembled supercapattery, GCD analysis was carried out for 4,000 cycles at a current density of 3 Ag^{-1} . The SnS@Ni/SnO₂/NF//AB/NF showed a satisfactory cyclic stability with capacity retention of 88% indicating that SnS@Ni/SnO₂/NF//AB/NF is highly reversible and suitable for long running energy storage application. The EIS before and after the cyclic stability study was carried out to investigate the changes in resistance over 4000 continuous charge discharge cycles. The Nyquist plot obtained from EIS technique is presented in inset of Fig. 9(c). A minimal increase in the ESR value (from 0.26 Ω to 0.28 $\Omega)$ was observed after 4,000 cycles which signifies a minimal degradation of the electrode surface or due to environmental effects on the device. Since the increase in the ESR was minimal, it does not have a significant impact on the cyclic performance and overall stability of the supercapattery. Thus, electrochemical analyses of the supercapattery show a promising overall performance for energy storage applications.

Conclusions

 $SnS@Ni/SnO_2$ has been fabricated successfully via hydrothermal technique and electrochemical analyses of the samples were conducted. XRD analysis confirmed the successful synthesis of the $SnS@Ni/SnO_2$ active material by observing the major peaks of XRD patterns. The optimized sample obtained from the study was the non-calcined $SnS@Ni/SnO_2$ with specific capacity of 319 C g⁻¹ at 2 Ag⁻¹. The bulky block like morphology upon calcination have restricted the active spots and concurrently increased the charge transfer resistance, resulting a decrease in the specific capacity of calcinated SnS@Ni/SnO2 electrode. In terms of the capacitive electrode, AB exhibited the highest specific capacitance of 381.19 Fg⁻¹ owing to the optimized conducting network formed for better percolation of the electrolyte. The assembled supercapattery exhibited maximum specific capacity of 157.08 C g^{-1} with maximum energy and power densities of 36.04 Wh kg^{-1} at 2 A g^{-1} and 12.28 kW kg^{-1} at 10 Ag⁻¹, respectively with capacity retention of 88% over 4000 cycles. In short, SnS@Ni/SnO2 as battery grade electrode in combination with activated carbonbased capacitive electrode containing 15 wt% acetylene black in supercapattery [SnS@Ni/SnO₂/NF//AB/NF] depicts a very good cyclic stability and electrochemical stability that is ideal for future energy storage devices.

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Author contributions

Davinder Singh: Writing – original draft, Validation, Data curation, Conceptualization. M. Pershaana: Writing – original draft, Methodology, Formal analysis, Data curation, Conceptualization. N.K. Farhana: Writing – review & editing, formal analysis, Validation. Shahid Bashir: Writing – original draft, Methodology, Data curation. S. Ramesh: Writing – review & editing, Writing – original draft, Methodology, Data curation, Conceptualization. K. Ramesh: Writing – review & editing, Writing – original draft, Supervision, Data curation.

Data availability

The datasets used and/or analysed during the current study are available from the corresponding author on reasonable request.

Declarations

Ethics approval and consent to participate Not applicable.

Consent for publication

Not applicable.

Competing interests

The authors declare that they have no known competing interests.

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