Investigations and improvement of Nickel Sulfide modified electrode material from single source precursor for energy storage application

C. Sambathkumar  
International Research Centre, Kalasalingam Academy of Research and Education

R. Ranjithkumar  
International Research Centre, Kalasalingam Academy of Research and Education

S. Ezhil Arasi  
International Research Centre, Kalasalingam Academy of Research and Education

A. Manikandan (✉ mkavath15@gmail.com)  
International Research Centre, Kalasalingam Academy of Research and Education

N. Nallamuthu  
International Research Centre, Kalasalingam Academy of Research and Education

M. Krishna Kumar  
International Research Centre, Kalasalingam Academy of Research and Education

A. Arivarasan  
International Research Centre, Kalasalingam Academy of Research and Education

P. Devendran  
International Research Centre, Kalasalingam Academy of Research and Education

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Abstract

High-performance energy storage electrode materials are emerging demand in near future for the construction of supercapacitor with high energy and power densities. Herein, Nickel (II) Diethylthiocarbamate was used as single source precursor for Nickel Sulphide (Ni$_9$S$_8$) two dimensional (2D) nanosheets preparation and hexadecylamine as shape directing agent via simple solvothermal method. The orthorhombic structure of Ni$_9$S$_8$ nanosheets was confirmed by X-ray diffraction (XRD) pattern. Scanning electron microscopy (SEM) and high resolution transmission electron microscopy (HRTEM) images revealed that as-prepared Ni$_9$S$_8$ nanoparticles possess sheet-like morphology. Besides, the thermal stability of Ni(DTC)$_2$ complex was studied by Thermo-gravimetric/Derivative thermo gravimetric(TG/DTG) with Differential scanning calorimetric (DSC) analysis. The electrochemical properties of Ni$_9$S$_8$ nanosheets was studied using galvanostatic charge-discharge (GCD) and cyclic voltammetry (CV) techniques. From the charge-discharge study of Ni$_9$S$_8$ nanosheets, a high specific capacitance of 281 F g$^{-1}$ was obtained at a current density of 1 A g$^{-1}$, and up to 82 % retentivity was achieved after 5000 cycles. Thus, the prepared Ni$_9$S$_8$ nanosheets could be one of the attractive potential active electrode materials for the application of supercapacitor.

1. Introduction

Recently, the demands for energy storage devices are highly expanding due to its worldwide utility. Present decades, the research area on energy storage devices development that uses nanoparticles (NPs) in it is interesting due to their size-dependent chemical and physical properties. The transition metal oxide (MO) and metal sulphide (MS) nanomaterials are being concentrated broadly due to extraordinary properties of optical, electrical, electronics, thermal, mechanical, and catalytic behavior. These characteristics are attributed due to their unique structures and size. The area of MS nanoparticles has wide applications such as superconductors, conversational solar energy devices, flat panel displays, fluorescence devices, electroluminescence devices, semiconductor devices, and photo-catalyst, etc., [1–3]. The two dimensional (2D) nanomaterials investigations are being done in semiconducting materials such as metal sulfides and metal oxides [4, 5]. Along with the MS family, Nickel sulfide semiconducting NPs include a potential candidate for diverse applications such as lithium-ion batteries, electrochemical supercapacitors, light-emitting diodes, photocatalysis, field-effect transistors and solar cell, etc., [3, 6–11]. Besides, various types of preparation methods are followed to prepare MS NPs with different structures and shapes (for example, sonochemical, reflex technique, sol-gel, microwave illumination, hydrothermal, and thermolysis technique) using a single source [3, 12–16]. Nickel sulfide nanoparticles have different crystalline structures, typically (NiS$_2$, Ni$_9$S$_8$, Ni$_7$S$_6$, Ni$_5$S$_2$, Ni$_5$S$_4$, Ni$_6$S$_5$, and NiS) have concentrated because of their high hypothetical limits and low cost [17, 18].

At present, the two possible solutions for energy demands are available in the marketplace; they are supercapacitors and hybrid batteries. Supercapacitor gives high energy density, but storage capacitance is low; consequently, the SCs do not be utilized in gadgets that require more storage capacitance. By this
way, in the current year supercapacitors have increased a lot of consideration instead of batteries. There are three kinds of supercapacitors such as (i) pseudocapacitors, (ii) EDLC (electrochemical double-layer capacitors), and (iii) hybrid capacitors [19]. Presently, SCs, as the best device for efficient power energy storage, have increased quickly expanding consideration for its powerful energy density, small size, more life cycles. SCs can be utilized in different fields, for example, hybrid storage device cars and other electric vehicles, the backup energy source in convenient electronic gadgets, and versatile hardware. Recently, Ni$_9$S$_8$ has standard capable electrode material in SCs. Also, it has exclusive properties like abundant oxidation and reduction activities, changing the magnetic phase, and more electrical conductivity, ecofriendly in nature, good electrochemical stability. The nickel sulfide materials are more excellent redox activity, high capacitance performance, and low cost, which are predictable to fulfill the expanding needs of the storage energy system [20–22].

Many researchers broadly concentrated on the utilization of single-source precursor-like metal complexes for the pure and perfect formation of MS with different architecture like 2D and 3D structured nanomaterials on a large scale. Moreover, single-source precursors are more stable, simple reaction conditions, and reducing by-products as well as less expensive. Arrangement of MS NPs has been broadly investigated using single-source precursors of the metal-dithiocarbamate complex [3, 7, 23–25]. Additionally, the MS materials demonstrated the great specific capacitance on the grounds, and the explanations define numerous redox states along with a variety of the progressive structure as well as pores nature of the material. The compositional MS materials with carbon-based complex give electrode material with high efficiency.

Here, Nickel dithiocarbamate [Ni(DTC)$_2$] complex has been utilized as single-source precursor for effective Ni$_9$S$_8$ 2D nano sheets synthesized, by using simple solvothermal technique. The Ni$_9$S$_8$ NSs were analyzed and confirmed with properties like phase-purity, good crystalline structure. Additionally, the prepared nanomaterials were analyzed with their electrochemical nature. Such as, cyclic voltammetry (CV), Chronopotentiometry (GCD) and electrochemical impedance spectroscopic (EIS) investigation was performed to study oxidation, reduction properties, charge-discharge mechanism and conductivity, respectively of the prepared Ni$_9$S$_8$ electrode materials.

### 2. Materials And Methods

#### 2.1. Materials

Ni(NO$_3$)$_2$ (Nickel nitrate), C$_5$H$_{10}$NNaS$_2$.3H$_2$O (Sodium diethyldithiocarbamate), C$_3$H$_7$NO (N, N-Dimethylformamide), C$_{16}$H$_{35}$N (Hexadecylamine), C$_2$H$_5$OH (ethanol), KOH (Potassium hydroxide), all precursors and solvents were purchased from Hi-media Laboratories Pvt. Ltd, India. Deionized (DI) water, CH$_3$OH (methanol), and N, N-Dimethylformamide were used as solvent for the entire reaction of [Ni(DTC)$_2$] complex formation and Ni$_9$S$_8$ NSs respectively.

#### 2.2. Preparation of [Ni(DTC)$_2$] complex
Nickel nitrate \([\text{Ni(NO}_3\text{)}_2]\) and sodium diethyldithiocarbamate \([\text{Na(DTC)}_2]\) were dissolved with 50 mL of DI water separately in 1:2 molar ratio. Both solution were mixed drop wise with constant stirring. The bright green color precipitate (PPT) was formed. The obtained sample were washed to remove un-reacted materials followed by ethanol wash, the single source precursor \((\text{Ni(DTC)}_2)\) were dried for 12 hrs at 70 °C [23, 24].

2.3. Preparation of nickel sulfide \((\text{Ni}_9\text{S}_8)\) NSs using \([\text{Ni(DTC)}_2]\) complex

Here, nickel diethyldithiocarbamate \([\text{Ni(DTC)}_2]\) complex and HDA were considered in weight ratio 1:1 quantity and dissolved in 100 ml of N, N-Dimethylformamide and the mixture was stirred about 10 minutes. These homogeneously mixed solutions were transferred to a double-necked round bottom flask and it was heated at 120 °C for 3 hrs by using solvothermal method. Subsequently, the PPT colour was observed with change from a bright green to a dark green colour. This colour change indicated the conversion of metal complex into metal sulfide and the graphical synthesis scheme were shown in Fig. 1. The product was washed several times using methanol to remove un-reactant and then the sample was dried in the hot oven at 70 °C for 12 hrs.

2.4. Instrumentation methods

The synthesized nickel sulfide NSs were examined with different analytical methods. The crystalline pattern was studied using Powder X-ray diffraction spectrum (Bruker-D8 advance ECO) instrument with 1.5406 Å (Cu-K\(\alpha\) radiation). The surface morphological study of NSs was performed with Scanning Electron Microscope technique, provided by way of EDS analysis. Fourier transform infrared spectrometer be utilizing the spectrometer (IR Tracer-100) with the constant range from 4000–400 cm\(^{-1}\) utilizing the KBr pellet method for functional group study. The structural morphological study of the prepared material performed with TEM instrument (model Jeol/JEM 2100). TG/DTG with DSC analysis was carried out on a Perkin-Elmer Thermo-gravimetric analysis. The electrochemical analysis of \(\text{Ni}_9\text{S}_8\) was investigated by the electrochemical workstation (CHI 6008e, USA).

2.5. Fabrication of working electrode

The charge-discharge, redox performance, and impedance investigation of synthesized \(\text{Ni}_9\text{S}_8\) nanosheets were deliberated utilizing a three-electrode system at room temperature. A \(\text{Ni}_9\text{S}_8\) modified electrode material, platinum wire, and Ag/AgCl was used as a working electrode, counter electrode, and reference electrode, respectively. 1 M KOH solution was utilized as the electrolyte medium. The \(\text{Ni}_9\text{S}_8\) modified electrode material, activated carbon as well as polyvinylidene fluoride binder ratio of 80:10:10 were considered and homogeneously mixed. Furthermore a drop of N-methyl-2-pyrrolidone (NMP) was added to the blend to make it as slurry and finally, it was applied as a small film utilizing Nickel foil of 0.01mm thick with 1cm\(^2\). It was dried at 60 °C and used for electrochemical analysis.
The specific capacitance values of the Ni$_9$S$_8$ modified working electrode has been calculated from cyclic voltammetry and chronopotentiometry techniques by using the formulae (1) and (2), respectively.

\[ C_{sp} \ (Fg^{-1}) = \frac{\int Idv}{mv \Delta V} \quad \text{........... (1)} \]
\[ C_{sp} \ (Fg^{-1}) = \frac{I \times \Delta t}{\Delta V \times m} \quad \text{........... (2)} \]

where, $C_{sp} \ (Fg^{-1})$ - specific capacity, $\int Idv \ (A)$ - integral area under the cyclic voltammetry curves, $v \ (mV \ s^{-1})$ - scan rate, $m \ (g)$ - mass of active electrode material, $\Delta V \ (V)$ - potential difference, $\Delta t \ (s)$ - discharge time, and $I \ (A)$ - constant discharge current.

3. Result And Discussion

3.1. Structural analysis

The powder X-ray diffraction patterns were performed for Ni$_9$S$_8$ NSs as shown in Fig. 2. The XRD pattern was recorded in the range of 2θ angle from 10 to 80°. The XRD pattern result revealed the perfect crystalline nature of Ni$_9$S$_8$ NSs and free from impurities. The existence diffraction peaks at 18.80°, 21.22°, 31.27°, and 41.35° are well matching with the hkl value of (002), (201), (222), and (150) respectively. Nickel sulfide nanosheets fits with the crystalline phases referring to the standard database of JCPDS card number 78-1886. All the XRD peaks confirmed the orthorhombic crystalline structure of nanosheets and the typical cell parameters, $a=9.335$, $b=11.21$, and $c=9.430$. The broad peaks indicate that the particle size is nano.

3.2. FT-IR Functional group analysis

Fig. 3 showed the FT-IR spectrum of prepared Ni$_9$S$_8$ NSs in this range of 4000 to 400 cm$^{-1}$. All peaks vibration frequencies were confirmed and closely matched with MS vibrations. Strong peaks observed at 3328 cm$^{-1}$ and 3284 cm$^{-1}$ N-H and C-H stretching vibration due to hexadecylamine and water molecules absorbed from the atmosphere [25–29]. The broad peak position at 2913 cm$^{-1}$ and 2841 cm$^{-1}$ showed stretching C-H vibration mode. The resultant small peak at 1374 cm$^{-1}$ to asymmetric extending vibration of O=C=O atoms. The strong and sharp peaks appeared in the range of 500 to 800 cm$^{-1}$ was due to metal rocking vibration of Nickel-Sulfide and extending the vibration at the range of 1111 cm$^{-1}$ refers to C-S extending mode [30–33].

3.3. Thermal stability of Ni(DTC)$_2$ metal complex
Thermal stability and behavior of the prepared metal complex \([\text{Ni(DTC)}_2]\) were examined by TG(DTA) and DSC were shown in Fig. 4 (a & b). The analysis was performed in temperature ranging from room temperature to 1000 °C in \(\text{N}_2\) atmosphere and at the rate of 10 °C/min. Two-step decomposition patterns were noticed in Fig. 4 (a) TGA curve. The first decomposition temperature range was observed between 163 °C to 205 °C which occurred in reason to the decomposition of unreacted sodium dithiocarbamate and weight loss of 2%. The second prominent weight loss was occurred between ~237 and 371 °C up to 85 % of weight loss was found and it was identified due to the single-source precursor \([\text{Ni(DTC)}_2]\) completely converted into Nickel sulfide (MS) and remaining ~15 % as pure nickel sulfide residue. Moreover, no one weight was found after the conversion of nickel sulfide and it was confirmed the thermal stability of nickel sulfide residue. The heat exchange was detected varying from 237 °C to 371.9 °C, recognized by the peak in the DTG curve at 352.4 °C. The corresponding DSC curve of the \(\text{Ni(DTC)}_2\) was shown in Fig. 4 (b). The second weight-loss region occurred between 237 °C to 371.9 °C and was accompanied by a significant endothermic heat flow, which corresponded to the decomposition of nickel complex to form nickel sulfide (\(\text{Ni}_9\text{S}_8\)). Hence, significant structural changes occurred at the range of the calcination temperature and it reviled that the thermal behaviour of \(\text{Ni(DTC)}_2\) and stability of nickel sulfides.

### 3.4. Morphological and elemental analysis

The surface morphological studies for the as-prepared nickel sulfide sample were characterized by SEM micrograph as shown in Fig. 5 (a, b) with diverse intensifications and it was look like two dimensional (2D) sheets morphology. The \(\text{Ni}_9\text{S}_8\) nano sheets are agglomerated in micrometer range and it is look feathers like structure. Also, the significant sheets like structure may occurred the influence of hexadecylamine as shape directing agent. The purity and formation of the \(\text{Ni}_9\text{S}_8\) NSs were confirmed with EDX spectrum and shown in Fig. 5 (c). The EDX spectrum reviled that, Ni and S elements are equally (1:1 ratio) presence in the \(\text{Ni}_9\text{S}_8\) NSs and the non-existence of other elements existence in the prepared sample as shown in Fig. 5c (insert). The standard weight percentage of Ni and S were found at 55.6% and 44.4% correspondingly. Further confirmation, the elemental mappings are examined for the prepared \(\text{Ni}_9\text{S}_8\) NSs (Fig. (d)). It is a clear evident that, there is no impurity are additional elements were found the randomly selected area mappings and this result coincides with XRD and EDX spectrum. Furthermore, It is confirmed that, the usage of \(\text{Ni(DTC)}_2\) complex as single source precursor for formation of high pure Nickel sulfide nanomaterials with large scale.

The structural morphology of the prepared \(\text{Ni}_9\text{S}_8\) NSs was characterized by HRTEM. Fig. 6 (a-c) showed the sheet like morphology of \(\text{Ni}_9\text{S}_8\) NSs. The average size of the nanosheets observed between 30 nm to few micrometers (mm) this result coincided with SEM and XRD analysis. Hexadecylamine had the vital role for capping and shape directing agent. Fig. 6 (d) displayed the selected area electron diffraction (SAED) pattern of the \(\text{Ni}_9\text{S}_8\) NSs. The SAED pattern clearly showed concentrically diffraction rings of orthorhombic crystalline structure and \(\text{Ni}_9\text{S}_8\) NSs verified the polycrystalline nature preferably distinct single crystal.
3.5. Electrochemical performance of Ni$_9$S$_8$ nanosheets

3.5.1. Cyclic voltammetry analysis

The prepared Ni$_9$S$_8$ NSs CV results were shown in Fig. 7 (a). The potential window of the Ni$_9$S$_8$ was fixed between 0 and 0.6 V. The electrochemical performance of Ni$_9$S$_8$ was analyzed by the 1M KOH electrolyte solution. The shape of CV results revealed the oxidation and reduction behavior of the prepared Ni$_9$S$_8$ sample. The redox reactions of Ni$_9$S$_8$ were recorded in the scan rate of 10 mVs$^{-1}$ to 100 mVs$^{-1}$. Besides, the CV all curves were a pair of redox peaks which indicated fast redox reaction [34]. While increasing the scan rates, the cyclic redox potential peak shifted which clearly represented the good electrochemical behavior of the Ni$_9$S$_8$ compound. The NiS compound redox reaction becomes [21].

\[
NiS + OH^- \rightarrow NiSOH + e^- \quad \text{......... (3)}
\]

\[
NiSOH + e^- \rightarrow NiSO + H_2O + e^- \quad \text{......... (4)}
\]

The outstanding electrochemical performance exposed due to Ni$^{2+}$ and Ni$^{3+}$ enabled the rich redox reactions of Ni$_9$S$_8$ NSs [35]. The calculated specific capacitance was shown in Fig. 7 (b) and also present in Table.1.

| Scan rate (mVs$^{-1}$) | Specific capacitance (Fg$^{-1}$) |
|-----------------------|---------------------------------|
| 10                    | 481                             |
| 25                    | 306.1                           |
| 50                    | 176.6                           |
| 75                    | 124.7                           |
| 100                   | 95                              |

Table: 1. The calculated specific capacitance of Ni$_9$S$_8$ nanoparticles from cyclic voltammetry results with different scan rates.

3.5.2. Chronopotentiometry analysis

The clear identification of the GCD (or) chronopotentiometry analysis of Ni$_9$S$_8$ was shown in Fig. 8 (a). The measuring potential window of the Ni$_9$S$_8$ was fixed ranging 0-0.5 V to exhibit a higher specific capacitance. The charge-discharge analysis of Ni$_9$S$_8$ compound had a non-linear shape which clearly
indicated the pseudocapacitance reactions. The anodic peak of Ni$_9$S$_8$ GCD analysis was in good agreement with the CV results. The specific capacitance was calculated with different current densities. The decreased specific capacitance was owing to active electrolyte ions diffusion on the increment of current densities. The outer active surface area of the electrode material acted as a charge storage area of the nickel sulfide compound [20]. Ni$_9$S$_8$ exhibited the IR drop in the charging and discharging analysis between ~0.42 and 0.5 V. The calculated specific capacitance of Ni$_9$S$_8$ at various current densities was displayed in Fig. 8 (b) and present in the Table. 2.

The high specific capacitance of Ni$_9$S$_8$ was 281 Fg$^{-1}$ due to provide a highly accessible area of the ion diffusion on the electrode species on the surface [20]. The cycle performance of Ni$_9$S$_8$ NSs was calculated as shown in Fig. 8 (c). The retention of the Ni$_9$S$_8$ electrode material was calculated from 10 Ag$^{-1}$, while the cycle's retention reached 82% after 5000 cycles. A. Sigh et al reported high electrochemical performance of asymmetric supercapacitor with MWCNT/Nickel Sulphide composite with graphene. In this, the reported results revealed high potential window of about 1.4 V with specific capacitance 181 Fg$^{-1}$ at the current density 1 Ag$^{-1}$. The cycle's retention became 92% after 1000 cycles [36]. The obtained results of Ni$_9$S$_8$ NSs were compared to existing results. The comparison of specific capacitance for various MS NPs was presented in Table 3.

**Table: 2**

| Current density A g$^{-1}$ | specific capacitance F g$^{-1}$ |
|---------------------------|-------------------------------|
| 1                         | 281                           |
| 2                         | 171.4                         |
| 3                         | 139.9                         |
| 4                         | 122                           |
3.5.3. Electrochemical Impedance spectroscopic analysis

The EIS spectrum of the Ni$_9$S$_8$ compound was studied in the frequency range 1 Hz to 1 MHz. The impedance spectrum was analyzed before and after cycles of the charge-discharge analysis shown in Fig. 8 (d). The impedance spectrum can be separated into three different regions. The first region was a high-frequency region, which reflected the internal resistance of the Ni$_9$S$_8$ electrode material. The second mid-frequency region consisted of indicating capacitance and resistance. The third region revealed the existence of Warburg resistance in the Ni$_9$S$_8$ electrode.

4. Conclusions

Nickel sulfide (Ni$_9$S$_8$) NSs were effectively prepared by simple solvothermal method with hexadecylamine as a capping agent. The Ni$_9$S$_8$ NSs properties/characteristics were studied with various analytical methods; orthorhombic crystalline nature was affirmed with powder XRD pattern and closely matched
with JCPDS Number 78-1886. The functional group stretching and bending vibrations confirmed the formation of Ni$_9$S$_8$ NSs using the FTIR analysis. The sheets like morphology, the elemental composition of Ni$_9$S$_8$ were confirmed by SEM images and EDS spectrum with mapping analysis, respectively. The obtained electrochemical result had good redox behavior as well as charge-discharge property. The chronopotentiometry result of Ni$_9$S$_8$ NSs exhibited high specific capacitance of 281 Fg$^{-1}$ at 1 Ag$^{-1}$ current density and the Ni$_9$S$_8$ electrode materials achieved retentivity of 82% after 5000 cycles. Finally, Ni$_9$S$_8$ nanosheets can be recommended for perfect electrode material for supercapacitor applications.

**Declarations**

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**References**

1. P.A. Ajibade, N.L. Botha, Synthesis and structural studies of copper sulfide nanocrystals. Results Phys. 6, 581–589 (2016). https://doi.org/https://doi.org/10.1016/j.rinp.2016.08.001

2. N. Khaorapapong, A. Ontam, M. Ogawa, Very slow formation of copper sulfide and cobalt sulfide nanoparticles in montmorillonite. Appl. Clay Sci. 51, 182–186 (2011). https://doi.org/https://doi.org/10.1016/j.clay.2010.10.030

3. P. Devendran, T. Alagesan, N. Nallamuthu, S. Asath Bahadur, K. Pandian, Single-precursor synthesis of sub-10 nm CdS nanoparticles embedded on graphene sheets nanocatalyst for active photodegradation under visible light. Appl. Surf. Sci. 534, 147614 (2020). https://doi.org/10.1016/j.apsusc.2020.147614

4. K. Kalantar-zadeh, J.Z. Ou, T. Daeneke, A. Mitchell, T. Sasaki, M.S. Fuhrer, Two dimensional and layered transition metal oxides. Appl. Mater. Today. 5, 73–89 (2016). https://doi.org/https://doi.org/10.1016/j.apmt.2016.09.012

5. M. Tanveer, C. Cao, Z. Ali, I. Aslam, F. Idrees, W.S. Khan, F.K. But, M. Tahir, N. Mahmood, Template free synthesis of CuS nanosheet-based hierarchical microspheres: an efficient natural light driven photocatalyst, CrystEngComm. 16 (2014) 5290–5300. https://doi.org/10.1039/C4CE00090K

6. A. Sarkar, A.K. Chakraborty, S. Bera, NiS/rGO nanohybrid: An excellent counter electrode for dye sensitized solar cell. Sol. Energy Mater. Sol. Cells. 182, 314–320 (2018). https://doi.org/10.1016/j.solmat.2018.03.026

7. P. Devendran, T. Alagesan, A. Manikandan, S. Asath Bahadur, M. Krishna Kumar, S. Rathinavel, K. Pandian, Sonochemical Synthesis of Bi$_2$S$_3$ Nanowires Using Single Source Precursor and Their
Electrochemical Activity, Nanosci. Nanotechnol. Lett. 8, 478–483 (2016). https://doi.org/10.1166/nnl.2016.2111

8. K. Jeyabanu, K. Sundaramahalingam, P. Devendran, A. Manikandan, N. Nallamuthu, Effect of electrical conductivity studies for CuS nanofillers mixed magnesium ion based PVA-PVP blend polymer solid electrolyte. Phys. B Condens. Matter. 572, 129–138 (2019). https://doi.org/10.1016/j.physb.2019.07.049

9. A. Shameem, P. Devendran, V. Siva, R. Packiaraj, N. Nallamuthu, S. Asath, Bahadur, Electrochemical performance and optimization of α-NiMoO₄ by different facile synthetic approach for supercapacitor application. J. Mater. Sci. Mater. Electron. 30, 3305–3315 (2019). https://doi.org/10.1007/s10854-018-00603-3

10. Z.-K. Tan, R.S. Moghaddam, M.L. Lai, P. Docampo, R. Higler, F. Deschler, M. Price, A. Sadhanala, L.M. Pazos, D. Credgington, F. Hanusch, T. Bein, H.J. Snaith, R.H. Friend, Bright light-emitting diodes based on organometal halide perovskite. Nat. Nanotechnol. 9, 687–692 (2014). https://doi.org/10.1038/nnano.2014.149

11. Q. Xu, Y. Liu, R. Su, L. Cai, B. Li, Y. Zhang, L. Zhang, Y. Wang, Y. Wang, N. Li, X. Gong, Z. Gu, Y. Chen, Y. Tan, C. Dong, T.S. Sreeprasad, Highly fluorescent Zn-doped carbon dots as Fenton reaction-based bio-sensors: an integrative experimental–theoretical consideration. Nanoscale. 8, 17919–17927 (2016). https://doi.org/10.1039/C6NR05434J

12. Y. Jiang, Y.-J. Zhu, G.-F. Cheng, Synthesis of Bi₂Se₃ Nanosheets by Microwave Heating Using an Ionic Liquid. Cryst. Growth Des. 6, 2174–2176 (2006). https://doi.org/10.1021/cg060219a

13. J. Cui, L. Wang, X. Yu, A simple and generalized heat-up method for the synthesis of metal sulfide nanocrystals. New J. Chem. 43, 16007–16011 (2019). https://doi.org/10.1039/C9NJ02644D

14. T.-W. Chen, U. Rajaji, S.-M. Chen, M. Govindasamy, S.S. Paul Selvin, S. Manavalan, R. Arumugam, Sonochemical synthesis of graphene oxide sheets supported Cu₂S nanodots for high sensitive electrochemical determination of caffeic acid in red wine and soft drinks. Compos. Part B Eng. 158, 419–427 (2019). https://doi.org/https://doi.org/10.1016/j.compositesb.2018.09.099

15. P. Devendran, T. Alagesan, K. Pandian, Single pot microwave synthesis of CdS nanoparticles in ionic liquid and their photocatalytic application, in: Asian J. Chem., 2013

16. P. Hu, Y. Cao, B. Lu, Flowerlike assemblies of Bi₂S₃ nanorods by solvothermal route and their electrochemical hydrogen storage performance. Mater. Lett. 106, 297–300 (2013). https://doi.org/https://doi.org/10.1016/j.matlet.2013.05.049

17. P. Luo, H. Zhang, L. Liu, Y. Zhang, J. Deng, C. Xu, N. Hu, Y. Wang, Targeted Synthesis of Unique Nickel Sulfide (NiS, NiS₂) Microarchitectures and the Applications for the Enhanced Water Splitting System. ACS Appl. Mater. Interfaces. 9, 2500–2508 (2017). https://doi.org/10.1021/acsami.6b13984

18. H.-C. Tao, X.-L. Yang, L.-L. Zhang, S.-B. Ni, One-step synthesis of nickel sulfide/N-doped graphene composite as anode materials for lithium ion batteries. J. Electroanal. Chem. 739, 36–42 (2015). https://doi.org/https://doi.org/10.1016/j.jelechem.2014.10.035
19. U.M. Patil, P.K. Katkar, S.J. Marje, C.D. Lokhande, S.C. Jun, Hydrous nickel sulphide nanoparticle decorated 3D graphene foam electrodes for enhanced supercapacitive performance of an asymmetric device. New J. Chem. 42, 20123–20130 (2018). https://doi.org/10.1039/c8nj04228d

20. P. Gaikar, S.P. Pawar, R.S. Mane, M. Nuashad, D.V. Shinde, Synthesis of nickel sulfide as a promising electrode material for pseudocapacitor application. RSC Adv. 6, 112589–112593 (2016). https://doi.org/10.1039/C6RA22606J

21. N.S. J.C.M. A. M. G., Facile microwave-hydrothermal synthesis of NiS nanostructures for supercapacitor applications. Appl. Surf. Sci. 449, 485–491 (2018). https://doi.org/10.1016/j.apsusc.2018.01.024

22. B. Guan, Y. Li, B. Yin, K. Liu, D. Wang, H. Zhang, C. Cheng, Synthesis of hierarchical NiS microflowers for high performance asymmetric supercapacitor. Chem. Eng. J. 308, 1165–1173 (2017). https://doi.org/10.1016/j.cej.2016.10.016

23. E. Sathiyaraj, S. Thirumaran, S. Ciattini, S. Selvanayagam, Synthesis and characterization of Ni(II) complexes with functionalized dithiocarbamates: New single source precursors for nickel sulfide and nickel-iron sulfide nanoparticles. Inorganica Chim. Acta. 498, 119162 (2019). https://doi.org/10.1016/j.ica.2019.119162

24. P. Devendran, T. Alagesan, T.R. Ravindran, K. Pandian, Synthesis of Spherical CdS Quantum Dots Using Cadmium Diethyldithiocarbamate as Single Source Precursor in Olive Oil Medium. Curr. Nanosci. 10, 302–307 (2014). https://doi.org/10.2174/15734137113096660117

25. E. Sathiyaraj, S. Thirumaran, Structural, morphological and optical properties of iron sulfide, cobalt sulfide, copper sulfide, zinc sulfide and copper-iron sulfide nanoparticles synthesized from single source precursors. Chem. Phys. Lett. 739, 136972 (2020). https://doi.org/10.1016/j.cplett.2019.136972

26. F. Ansari, A. Sobhani, M. Salavati-Niasari, Green synthesis of magnetic chitosan nanocomposites by a new sol–gel auto-combustion method. J. Magn. Magn. Mater. 410, 27–33 (2016). https://doi.org/10.1016/j.jmmm.2016.03.014

27. Y. Fazli, S. Mahdi Pourmortazavi, I. Kohsari, M. Sadeghpur, Electrochemical synthesis and structure characterization of nickel sulfide nanoparticles. Mater. Sci. Semicond. Process. 27, 362–367 (2014). https://doi.org/https://doi.org/10.1016/j.mssp.2014.07.013

28. A. Sobhani, M. Salavati-Niasari, Synthesis, characterization, optical and magnetic properties of a nickel sulfide series by three different methods. Superlattices Microstruct. 59, 1–12 (2013). https://doi.org/https://doi.org/10.1016/j.spmi.2013.03.018

29. O.O. Baylayeva, A.A. Azizov, M.B. Muradov, A.M. Maharramov, G.M. Eyvazova, R.J. Gasimov, Z.X. Dadashov, Effect of thermal annealing on the properties of nickel sulfide nanostructures: Structural phase transition. Mater. Sci. Semicond. Process. 64, 130–136 (2017). https://doi.org/10.1016/j.mssp.2017.03.021

30. R. Karthikeyan, D. Thangaraju, N. Prakash, Y. Hayakawa, Single-step synthesis and catalytic activity of structure-controlled nickel sulfide nanoparticles. CrystEngComm. 17, 5431–5439 (2015).
31. S. Pan, J. Zhu, X. Liu, Preparation, electrochemical properties, and adsorption kinetics of \( \text{Ni}_3\text{S}_2/\text{graphene} \) nanocomposites using alkylidithiocarbonatio complexes of nickel(ii) as single-source precursors. New J. Chem. 37, 654–662 (2013). https://doi.org/10.1039/C2NJ40854F

32. H.S. Mahdi, A. Parveen, A. Azam, Structural and photoluminescence properties of Ni doped CdS nanoparticles synthesis by sol gel method, AIP Conf. Proc. 1953 (2018) 30031. https://doi.org/10.1063/1.5032366

33. G.S. Lotey, S. Guleria, Crystallographic, magnetic and optical analysis of Ni-doped CdS dilute magnetic semiconducting nanoparticles. J. Mater. Sci. Mater. Electron. 26, 7715–7718 (2015). https://doi.org/10.1007/s10854-015-3413-5

34. J. Xu, L. Wang, J. Zhang, J. Qian, J. Liu, Z. Zhang, H. Zhang, X. Liu, Fabrication of porous double-urchin-like MgCo\(_2\)O\(_4\) hierarchical architectures for high-rate supercapacitors. J. Alloys Compd. 688, 933–938 (2016). https://doi.org/10.1016/j.jallcom.2016.07.250

35. T.F. Hung, Z.W. Yin, S.B. Betzler, W. Zheng, J. Yang, H. Zheng, Nickel sulfide nanostructures prepared by laser irradiation for efficient electrocatalytic hydrogen evolution reaction and supercapacitors. Chem. Eng. J. 367, 115–122 (2019). https://doi.org/10.1016/j.cej.2019.02.136

36. A. Singh, A.J. Roberts, R.C.T. Slade, A. Chandra, High electrochemical performance in asymmetric supercapacitors using MWCNT/nickel sulfide composite and graphene nanoplatelets as electrodes. J. Mater. Chem. A. 2, 16723–16730 (2014). https://doi.org/10.1039/C4TA02870H

37. B. Li, Y. Hu, J. Li, M. Liu, L. Kong, Y. Hu, L. Kang, Mechanical Alloying Synthesis of Co\(_9\)S\(_8\) Particles as Materials for Super capacitors, Metals (Basel). 6 (2016) 142. https://doi.org/10.3390/met6060142

38. A.K. Noordeen, S. Sambasivam, S. Chinnasamy, J. Ramasamy, T. Subramani, Hierarchical Flower Structured Bi\(_2\)S\(_3\)/Reduced Graphene Oxide Nanocomposite for High Electrochemical Performance. J. Inorg. Organomet. Polym Mater. 28, 73–83 (2018). https://doi.org/10.1007/s10904-017-0701-y

39. K. Liang, C. Wang, X. Xu, J. Leng, H. Ma, Capacitive and photocatalytic performance of Bi\(_2\)S\(_3\) nanostructures synthesized by solvothermal method. Phys. Lett. A. 381, 652–657 (2017). https://doi.org/10.1016/j.physleta.2016.12.005

40. N. Nair, B.R. Sankapal, Cationic-exchange approach for conversion of two dimensional CdS to two dimensional Ag\(_2\)S nanowires with an intermediate core–shell nanostructure towards supercapacitor application. New J. Chem. 40, 10144–10152 (2016). https://doi.org/10.1039/C6NJ02411D

41. F. Yu, V.T. Tiong, L. Pang, R. Zhou, X. Wang, E.R. Waclawik, K. (Ken) H. Ostrikov, Wang, Flower-like Cu\(_5\)Sn\(_2\)S\(_7\)/ZnS nanocomposite for high performance supercapacitor. Chinese Chem. Lett. 30, 1115–1120 (2019). https://doi.org/10.1016/j.cclet.2019.01.004

42. K. Krishnamoorthy, P. Pazhamalai, S.J. Kim, Ruthenium sulfide nanoparticles as a new pseudocapacitive material for supercapacitor. Electrochim. Acta 227, 85–94 (2017). https://doi.org/10.1016/j.electacta.2016.12.171
Figures

Figure 1

Schematic representation of preparation of metal complex and Ni9S8 nanosheets

(a) \( \text{Ni}_9\text{S}_8 \)

(b) jcpds:78-1886
Figure 2

Powder XRD pattern of prepared Ni9S8 nanosheets

Figure 3

Representative FTIR spectra of Ni9S8 NSs
Figure 4

(a) Thermogravimetric (TGA) and derivative thermogravimetric (DTG) curve, (b) Differential scanning calorimetric (DSC) curve of the as synthesized [Ni(DTC)2] complex.
Figure 5

(a, b) SEM image, (c) EDS spectrum and (d) mapping images of prepared Ni9S8 NSs
Figure 6

(a-c) HR-TEM images of Ni9S8 nanosheets with high magnification with different areas, (d) SAED pattern
Figure 7

(a) CV curves at different scan rates, (b) Specific capacitance vs scan rate
Figure 8

(a) GCD curves at different current densities, (b) Specific capacitance vs current density, (c) Specific capacitance plot of Ni9S8 NSs up to 5000 cycles, (d) EIS spectra of Ni9S8 NSs