Synthesis of Spherical NiS_2 Nanoparticles as Electrode Materials for Supercapacitor Applications

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Abstract

The present study efficiently generated nickel disulfide (NiS_2) nanoparticles using the hydrothermal treatment. X-ray diffraction pattern (XRD) was employed for assessing the crystalline phases and the structural properties. The surface of the NiS_2 material is found to be rough with spherical morphology with particle size of 100-150 nm, confirmed by FESEM microscopic images. Surface area characteristics were assessed using BET analysis and found to be having high surface area and porosity. Utilizing electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV) method and galvanostatic charging and discharging (GCD) studies of the NiS_2 electrode in a 6 M aqueous KOH electrolyte, the electrochemical features have been studied. The resulting NiS_2 nanoparticles displayed excellent performance with a high specific capacitance of 1406 Fg^{-1} at 1 Ag^{-1} and a high cycling stability of 78% of the starting value across 5000 cycles with Columbic efficiency of 98%. The end product illustrates a simple, comprehensive, and practical approach of generating an efficient material for supercapacitor applications.

Keywords: *NiS_2, Supercapacitor, Hydrothermal method, Specific capacitance, Electrochemical studies*

1.0Introduction

With an upsurge in the demand for energy and the widespread use of petroleum and other fossil fuels, high-performance supercapacitors have captured the fascination among researchers owing to their considerable high power density, rapid charging and discharging capacity, and excellent cyclic stability [1-2]. Supercapacitors can be categorized into two distinct categories depending on their energy storage processes: electric double-layer capacitors and faradaic pseudo-capacitors. Due to a swift and efficient charging-discharging electrochemical process arising

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on the surface of the electrode, pseudo capacitors could possess greater specific capacitance values and energy density than electric double-layer capacitors [3, 4]Additionally, although the effective electronegativity of transition metallic sulfides tends to be lower than that of oxides of transition. metals, their electrochemical reactions and conductance remained noticeably better in contrast to oxides [5]. Furthermore, the material's physical and thermal endurance surpasses oxides. Also, given the efficient combination of various valence configurations of nickel sulfide, these compounds possess sites that are more active than oxides of metals all through the course of the reaction, boosting the electrochemical reactions. As a consequence, when compared to a typical metallic oxide electrodes, metallic sulfides such as NiS_2 have drawn curiosity of researchers because of their outstanding electrical conductivity, rate efficiency, and specific capacities[6]. However, in electrochemical devices, sulphur-rich materials are frequently used as electrodes. Since sulphur has significant electro-negativity when compared with nickel Maximum theoretical capacity, great cycle stability, minimal charge transfer resistance, outstanding electronic conductivity, and high reductive activity have been observed in the sulphur-rich nickel sulphide phase. Nickel is an inexpensive, non-hazardous, and ecologically safe material[7, 8] due to various parameters, such as the electrode's varied phases, surface porousness, electrical conductivity, morphological features and so on. Electrolytic ions are able to penetrate the external layer of electrodes owing to the significant pore volume of nanomaterial, resulting in higher electrochemical activity[9]. The electrical, optical, and magnetic features of NiS_2, a pyrite framework, are highly remarkable. Yet, because of their inherent chemical structure, it has been challenging to control the production of uniform NiS_2 nanoparticles [10, 11]. The hydrothermal approach is employed in the process of synthesis of NiS_2 nanoparticles with the goal of enhancing the electrochemical efficiency of the material. In the work of Fu et al., the Ni_3S_2 nanosheet arrays formed honeycomb structures and exhibited a specific capacitance of 151.2 $mAhg^{-1}$ at a current density of 3 Ag^{-1} [12]. The specific capacitance of structured flower-like -NiS at 2 Ag^{-1} measured to be 857.76 Fg^{-1}, as reported by Yang et al[13]. The specific capacitance of 695 Fg^{-1} has been observed by Pang et al. in NiS_2 nanocubes produced through a microwave-assisted process at a current density of 1.25 Ag^{-1} [14]. These investigations made an appealing argument of employing nickel sulphide as an electrode material in supercapacitors. A comprehensive description of a single-step hydrothermal chemical synthesis of NiS_2 nanoparticles has been

demonstrated here. For confirmation of the development of NiS_2, the structural and morphological characterizations were carried out.

To investigate both physical and electrochemical characteristics, multiple methods such as XRD, FESEM, N_2 adsorption-desorption isotherms, Electron impedance spectroscopy (EIS), galvanostatic charging and discharging (GCD) and Cyclic Voltammetry (CV) were employed.

2.0 Experimental

A. Chemicals Used

For the synthesis of NiS_2 nanoparticles, analytical grade chemicals such Nickel (II) chloride ($NiCl_2.6H_2O$) and Sodium sulphide (Na_2S) were used without further purification. For the preparation of working electrode, N-methyl 2 pyrrolidone (NMP) and polyvinylidene fluoride (PVDF,)) were used as solvent and binder, respectively. The investigation of electrochemical properties involved the utilization of potassium hydroxide as the electrolyte.

B. Preparation of NiS2 nanoparticles and electrode fabrication

Hydrothermal method was employed for the synthesis of NiS_2 nanoparticles. 2.6 g of $NiCl_2$ and 0.86 g of Na_2S were dissolved in 80ml of distilled water under constant stirring. The resulting solution was transferred to a Teflon lined autoclave with 100ml capacity. The autoclave was then placed in a hot air over at 140^oC for 2 h. Then the autoclave was cooled to room temperature naturally and the resulting black precipitate was washed with distilled water and acetone, dried at 80^oC in hot air oven for nearly 2 h. The dried product was ground in an agate mortar and was utilized for further characterization studies. To assess the electrochemical characteristics of the NiS_2 electrode material, a working electrode was prepared. This involved coating a slurry containing the active material, carbon black, and PVDF (with PVDF dissolved in NMP solvent) in the ratio 85:10:5 (wt. %) onto a carbon Toray sheet. Subsequently, the electrode was dried at 80°C for 2 h in a hot-air oven, resulting in an approximate loading of 1 mg of active material.

3.0 Material And Electrochemical Characterization

The technique of powder X-ray diffraction (PXRD) with Cu k irradiation ($\boldsymbol{\lambda}$= 1.5418 A^0) by Rigaku SmartLab was employed for assessing the crystalline structure and chemical constituents of the materials. Carl Zeiss, Germany, was used for field-emission scanning microscopy (FE-SEM). Using the technique known as Brunauer-Emmett-Teller, specific area of the material was examined using Autosorb IQ-XR-XR, Austria. A three-

electrode setup in 6 M aqueous KOH electrolyte was utilized for all electrochemical evaluations, with a Platinum needle serving as a counter electrode and an saturated calomel electrode functioning as the reference electrode. A CHI 660D electrochemical workstation was utilized for carrying out tests using cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), and electrochemical impedance spectroscopy in the frequency range 10^{-2}- 10^{6} Hz.

C. Equations

The specific capacitance of electrode material was calculated using equation (1)

$$C_S = \frac{I * t}{m * \Delta v} \qquad (1)$$

where "I" is the current density (Ag^{-1}) "t" represents discharging time (s) "m" is the mass of active material loaded on working electrode (g) and Δv is the potential window (V).

Coulombic efficiency is given by equation (2)

$$\eta = \frac{t_d}{t_c} * 100 \qquad (2)$$

where t_d is the discharging time and t_c represents charging time in galvanostatic charging and discharging curves.

4.0 Results and Discussions

D. Structural and Morphological Characteristics

Fig. 1 displays the wide-ranging XRD measurements of the generated material. The sample that was generated is NiS_2, based on all of the diffraction peak values, which are referenced using JCPDS data card no. 89-3058.The peak values of diffraction (2Θ) have been mapped to the (111), (200), (210), (211), (220),(311),(023),(322) and (131) planes, respectively, at 27.44°, 31.45°, 34.86°, 38.5°, 45.51°, 54.01°, 56.23°, 58.75° and 75.93°.The prepared sample NiS_2 exhibits a cubic crystal arrangement and with a space group of (205) Pa-3. The lattice parameter values are a = b = c = 5.2 A °. Fig. 2(a) and 2(b) shows that the material being studied is composed of regular spherical particles of diameter 100-150 nm with polycrystalline structure, as seen in the standard low-magnification SEM (scanning electron microscopy) photograph. Additionally, these outcomes reveal that the material is extremely crystalline in nature. NiS_2 spherical nanoparticles have a rough texture, a

pore-like, textured surface which provides huge surface areas and provides microscopic molecular and electrolytic accessibility.

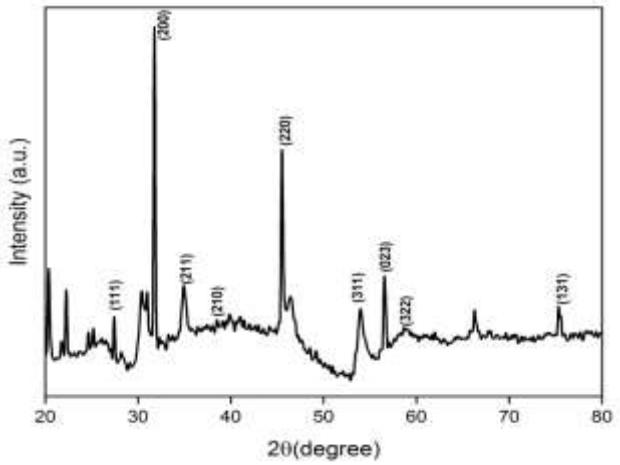

Fig. 1. X-Ray diffraction pattern of NiS_2 nanoparticles.

For the purpose of investigating the chemical composition of the material, the energy dispersive spectroscopic examination (EDS) for nickel and sulfur has been performed. The material was composed of the nickel and sulphur components as seen in Fig 2(c). Thus, the synthesis of NiS_2 material is successfully carried out, as indicated by the chemical component Ni and S with atomic proportion of 65.6:34.4.

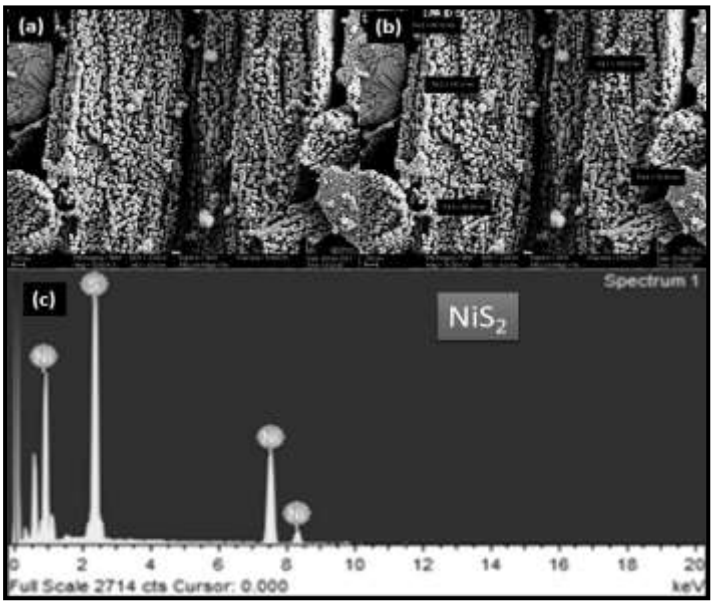

Fig. 2. (a) and (b) FESEM images of NiS_2 nanoparticles (c) Electron dispersive spectrum of NiS_2 nanoparticles.

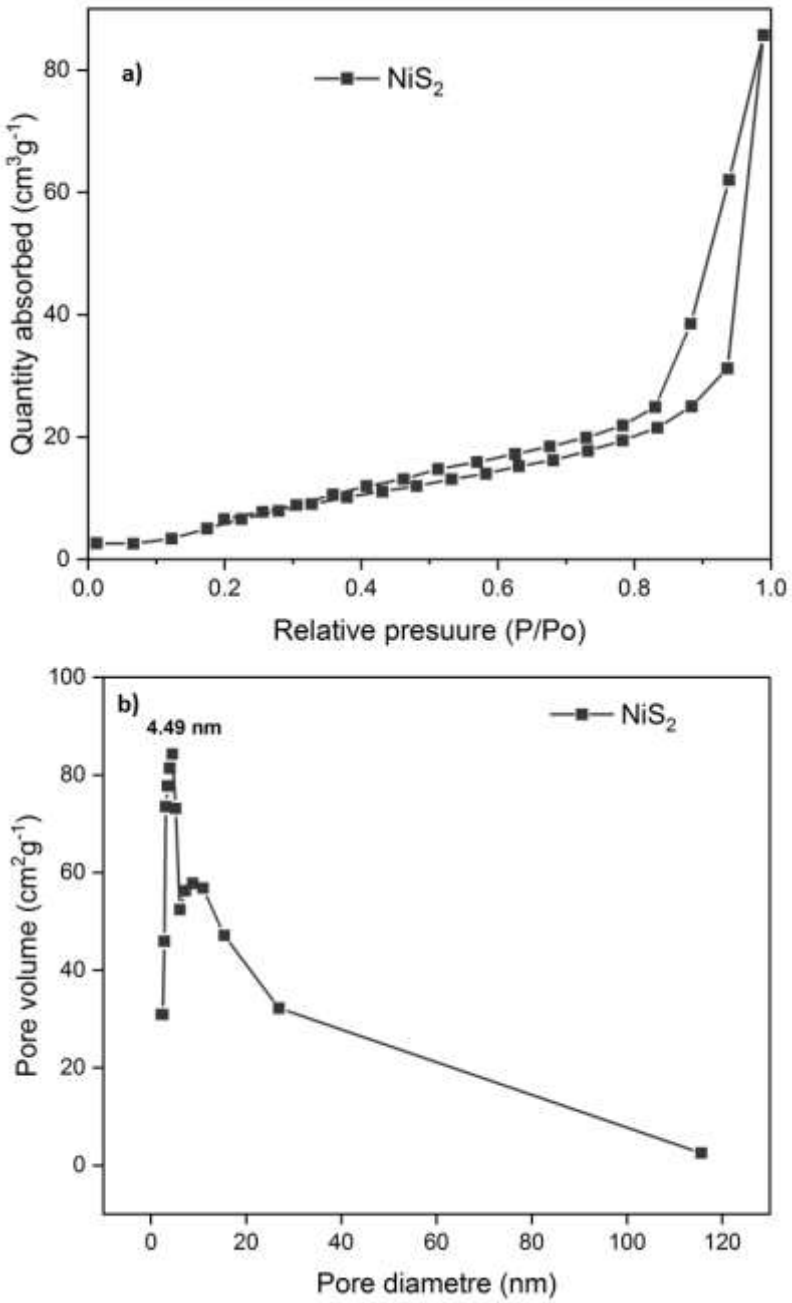

Fig. 3. (a) N_2 absorption desorption isotherm of NiS_2 nanoparticles, (b) Pore distribution based on BJH analysis of NiS_2.

In utilizing the electrode materials in supercapacitors, specific surface area (SSA) is essential and critical for electrochemical properties. Based on the Brunauer-Emmett-Teller (BET) adsorption-desorption isotherm, the

specific area of surface and porosity framework of NiS_2 spherical nanoparticles were determined. At a relative pressure (P/P_0) of 0.2-1, nitrogen (N_2) adsorption-desorption profiles exhibited a standard type 4 isotherms with a characteristic hysteresis cycle which highlighted their structured mesoporous porous framework as shown in Fig 3(a). It was found that NiS_2 possessed BET surface area of 68.67 m^2g^{-1}. From Barrett Joyner-Halenda (BJH) analysis, the associated pore size variation was determined. Based on the BJH curve, pure spherical NiS_2 has an elementary pores peak around 4.49 nm indicates the presence of a mesoporous structure for NiS_2 nanomaterial.

E. Electrochemical Studies

The electrochemical behavior of the as synthesized electrodes was assessed through cyclic voltammetry (CV), galvanostatic charging discharging (GCD) and electrochemical impedance spectroscopy (EIS) analyses in a 6M KOH electrolyte. The electrochemical activity of the nickel sulfide nanostructures was characterized using CV tests. In the Fig. 4(a), CV curves of the NiS_2 electrode are presented for various scan rates from 10mVs^{-1} to 90 mVs^{-1}. Each CV curve displays a pair of redox peaks, indicating that the measured capacitance primarily relies on the redox mechanism. The robust anodic peak observed at -0.04 along with its corresponding cathodic peak at -0.35V can be attributed to the redox reactions involving $Ni^{2+/}Ni^{3+}$[15]. As the scan rate is raised there is an associated augmentation in the redox current. This heightened current response indicates that the kinetics of interfacial faradic redox reactions and the velocities of electronic/ionic transport are sufficiently rapid, showcasing enhanced speed[16]. The CVs are almost symmetric, suggesting good reversibility of the oxidation and reduction processes and high efficiency. With an increase in the scan rate, the oxidation peak moves towards higher potentials, and concurrently, the reduction peak shifts in the opposite direction. This shift could be attributed to the amplified internal resistance of the active material[15]. GCD experiments were conducted to explore the specific capacitance and rate capability of NiS_2 electrodes. GCD behaviours were documented across various current densities spanning from 1 to 7 A/g, in the potential range of 0 to 0.5 V, respectively as illustrated in Fig 4 (b).

The symmetrical nature of the charging/discharging curves indicated a favourable trait, suggesting that the NiS_2 electrodes possess exceptional electrochemical capabilities and exhibit a reversible redox process[17]. The value of specific capacitances are 1406, 926, 881, 820, 806, 674 and 580 Fg^{-1} at 1- 7 Ag^{-1} respectively. The graphs depicting the relationship

between specific capacitance, capacitance retention, and current density are presented in the Fig 5 (a) and (b).The specific capacitance typically diminishes with an elevation in current density. This phenomenon could be attributed to factors like heightened internal resistance and constrained ion diffusion kinetics. When current densities increase, the rapid charging and discharging rates can cause voltage drops across the electrode-electrolyte interface, along with hindered ion diffusion within the electrode material Cycling tests for evaluating long term stability were carried out at 15 A/g for 5000 cycles of charge-discharge in Fig 6(a). NiS_2 exhibited 78% capacitance retention and 98% coulombic efficiency after 5000 charging and discharging cycles. To determine the electrical. Conductivity, EIS was conducted on NiS_2 electrodes at room temperature.

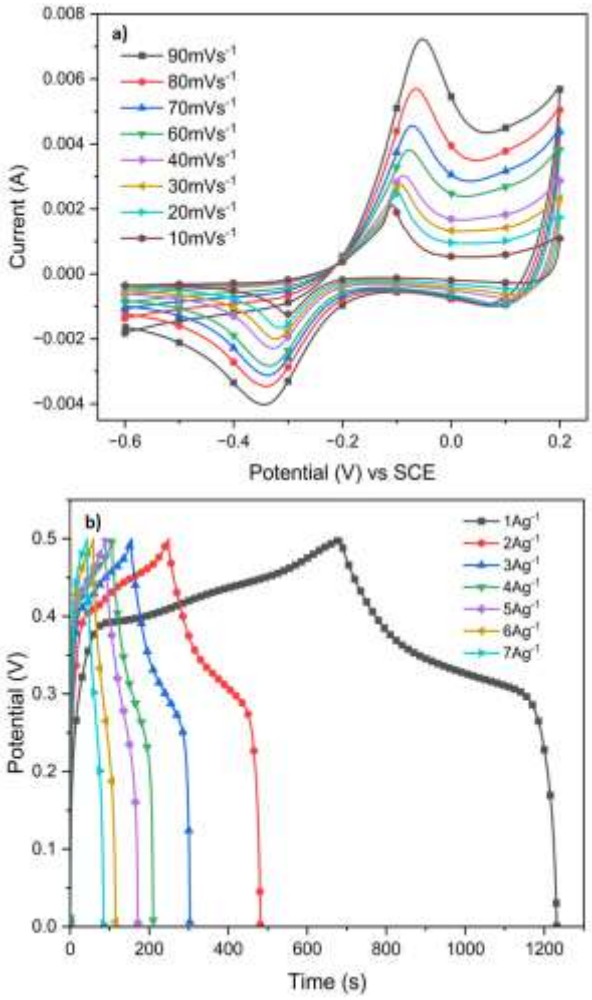

Fig. 4. a) Cyclic voltammagram of NiS_2 electrodes at scan rates from 10-90 mVS^{-1} b) Galvanostatic charging and discharging curves of NiS_2 electrode at different current density from 1-7 $Ag^{-1.}$

The frequency range for the analysis spanned from 0.01 to 10^5 Hz, with measurements taken under open-circuit conditions and the corresponding Nyquist plot is depicted in Fig 6(a) . Within the Nyquist plot, the solution resistance (R_s) manifests as the intercept on the Z' axis in the high-frequency segment which is a combinational resistance of ionic resistance of electrolyte, intrinsic resistance of substrate, and contact resistance at the active material/current collector interface[18]. The diameter of the semi-circle indicates the charge-transfer resistance (R_{ct}) at the interface between the electrolyte and electrode which was caused by the Faradic reactions and the double-layer capacitance on the grain surface. It was observed that NiS_2 has R_s= 1.58Ω and R_{ct} =1.13Ω.Lower R_s and R_{ct} values imply good capacity performance and remarkable charge transfer rate[19].

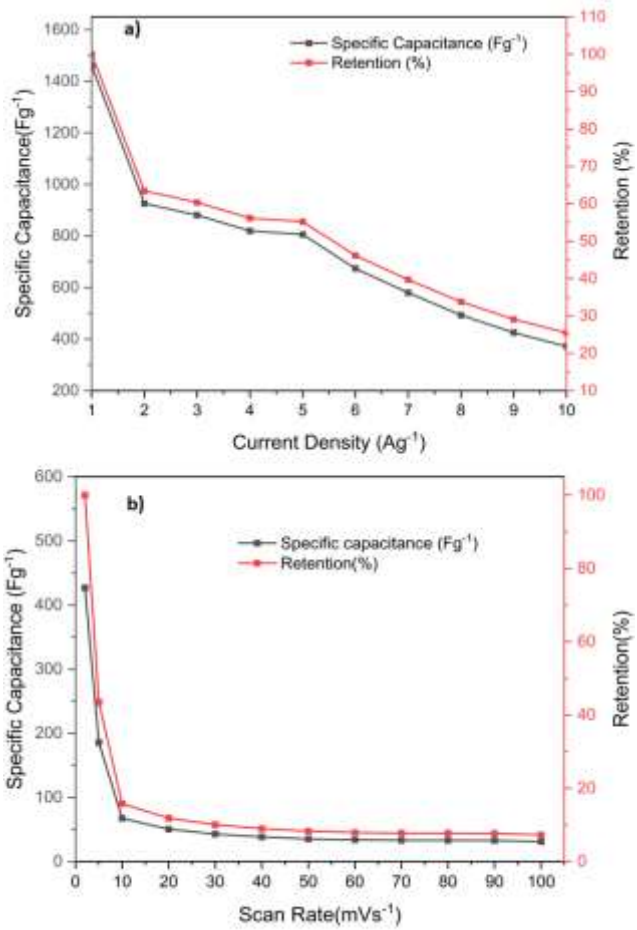

Fig. 5. a) Graph representing current density vs Specific capacitance of NiS_2 electrode b) graph representing scan rate vs Specific capacitance of NiS_2 electrode with rate of capacitance retention

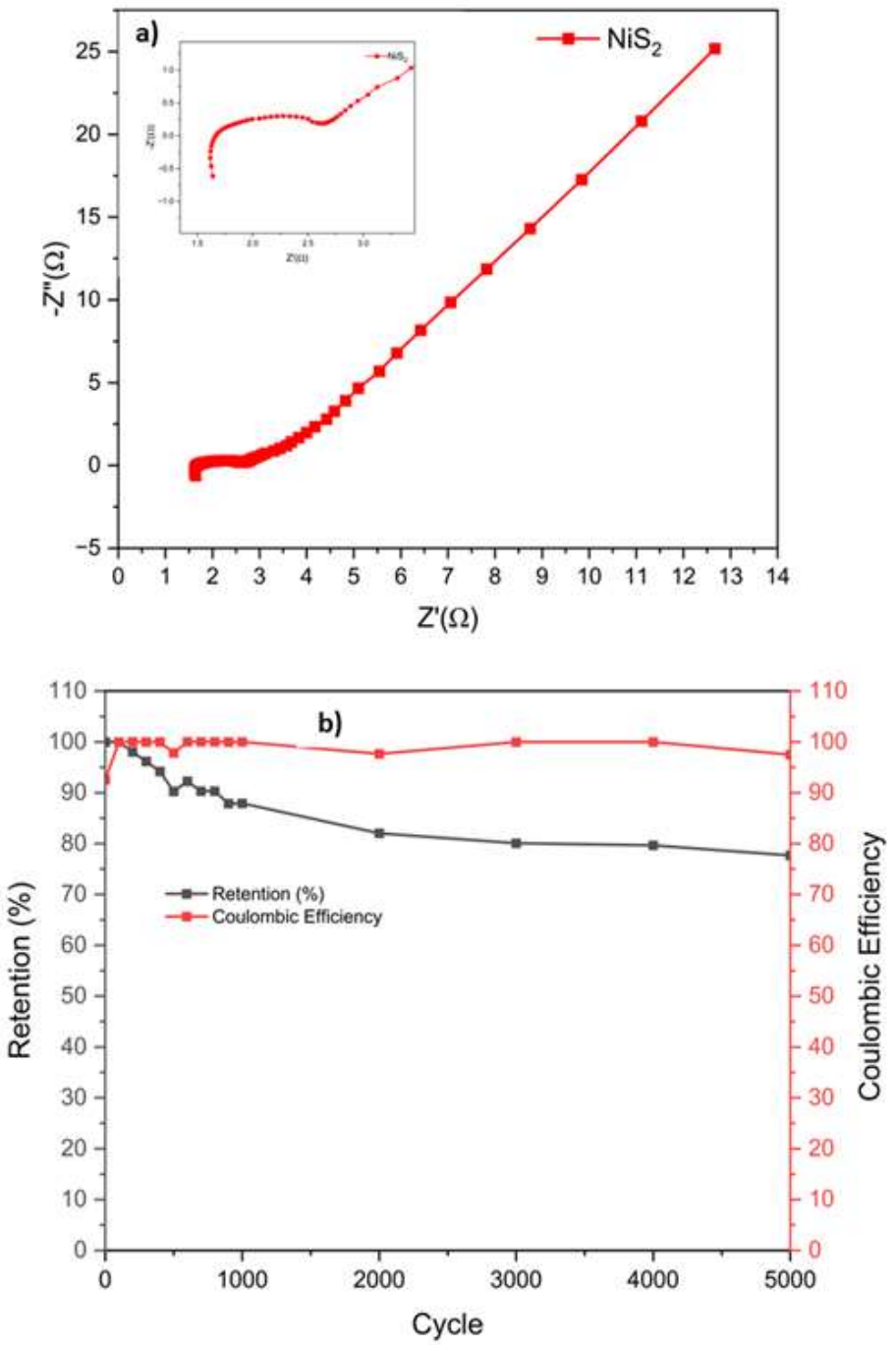

Fig. 6. a) Nyquist plot of NiS_2 electrode in the frequency range 10^{-2} to 10^6 Hz. b) Graph representing Cycle number verses retention and columbic efficiency of NiS_2 electrode.

The electrochemical performance and fabrication process for numerous NiS_2 based materials are analysed in Table 1. The findings demonstrate that the as-obtained NiS_2 spherical nanoparticles have an enhanced specific capacitance, highest rate efficiency and exceptional cycling reliability. The reduced diffusion channel and material synergy are accountable for the enhanced characteristics.

Table 1. Electrochemical properties of NiS2 based materials in three electrode system

Material	Electrolyte (KOH), Molarity	Specific capacitance (Fg^{-1}) at current density (Ag^{-1}) , cyclic stability (%) and No of cycles	References
NiS_2/graphene	6	478.@1 , 0.5, 89.3%, 2000	[16]
NiS_2 nanocubes	3	695,@ 1.25, 93.4%, 3000	[14]
NiS_2 square rod	6	1020.2 @ 1,93.5 %,1000	[20]
pyrite NiS_2	6	1072.6 @ 1,78 %,1000	[21]
NiS_2/rGO	2	565 @1,95.3%,10000	[22]
NiS_2/CNT	6	620 @ 1, 49.19 %,1000	[23]
NiS_2 spherical nanoparticles	6	1406 @1,78 %,5000	Our work

5.0 Conclusion

In the present study, hydrothermal synthesis of mesoporous NiS_2 nanoparticles was successfully achieved. The samples that were generated had spherical shaped nanoparticles with mean sizes for crystallite of 100-150 nm assessed using SEM images. The NiS_2 spherical nanoparticles showed enhanced electrochemical potential owing to its high specific surface area and large pore width confirmed by BET analysis. The electrochemical properties of NiS_2 electrodes were carried out in 6 M KOH which exhibited a high capacitance of 1406 Fg^{-1} at current density 1 Ag^{-1} with capacitance retention of 78% after the electrode demonstrated columbic efficiency of 98% in 5000 cycles. The superior electrochemical performance of NiS_2 nanoparticles demonstrates that the material studied in this work is a promising candidate for supercapacitor energy storage device application.

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