

RESEARCH ARTICLE

Synthesis of NiSe₂ Materials Directly on Ni Foam using Microwave-Assisted Technique and Employing as Electrode Material in Supercapacitors

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ABSTRACT

As the world's population grows, the energy crisis is becoming an increasingly severe problem, driving the need for energy storage. This demand is a significant driver for innovation and development in the energy sector. Clean and sustainable energy research focuses on two areas: renewable resources and high-performance energy storage systems. Today's energy systems provide large amounts of electricity generation, but the desired results cannot be achieved in the energy storage process. There is an urgent need for high-capacity and efficient energy storage devices. Supercapacitors are one of the most promising technologies for energy storage. They have competitive features such as high power density, excellent cycle stability, and short charge/discharge time. This study demonstrates the potential usage of NiSe₂ in supercapacitor applications as cathode material. In an experimentally novel approach, NiSe₂ on nickel foam was synthesized by a fast, simple, and inexpensive microwave-assisted method in the presence of selenium salt. In this route, nickel foam was employed as both nickel source and substrate. Furthermore, the electrochemical properties of the prepared NiSe₂ cathodes were investigated in three electrodes system. As a result, NiSe₂ obtained in 45 minutes delivers a high capacitance of 3.3 F/cm² at a high current density of 5 mA/cm².

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1. Introduction

The anticipated depletion of fossil fuels and the environmental consequences associated with greenhouse gas emissions have prompted a global surge in demand for the advancement of renewable energy sources, including solar, hydro, and wind energies (Bekhit et al., 2022a). Given the pollution effects of fossil fuels and concerns about global

warming, there has been significant interest in lithium-ion batteries (LIBs) and supercapacitors (SCs) as energy storage devices. These technologies hold the potential to serve as primary energy sources for portable devices and show promise for applications in electric cars as well as large-scale electric networks (Shao et al., 2018; Bekhit et al., 2022b). Supercapacitors are one of the most promising technologies for energy storage systems. They have competitive features such as

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high power density, excellent cycle stability, and short charge/discharge time. It also attracts attention with its high specific power, long life, and environmental friendliness (Zhang & Zhao, 2012; Mu et al., 2017).

Supercapacitors are analyzed under two main categories: electrical double-layer capacitors (EDLCs) and pseudo capacitors. In pseudo capacitors, charge storage is realized through faradaic surface redox reactions, and charge is transferred across the interface. Since these redox reactions occur slower than bilayer formation, pseudo capacitors provide higher energy density and higher specific capacitance values compared to EDLCs. Pseudo capacitors utilize materials that exhibit pseudocapacitance, such as transition metal oxides/sulfides and conducting polymers (Tang et al., 2015).

Materials with high surface area are being investigated as supercapacitor electrode materials with excellent properties in a three-electrode system. Moreover, supercapacitor devices with high energy density pave the way for practical applications of these materials.

Nowadays, due to their low band gap and high conductivity properties, researchers focus on materials such as NiO, Ni(OH)₂, and NiS_x for high-performance supercapacitor electrode materials (Wei et al., 2014; Wu et al., 2014).

The chemical elements Oxygen (O), Sulfur (S), and Selenium (Se) are close neighbors in the sixth leading group of the periodic table and exhibit similar properties (Mi et al., 2012). Se shows a more pronounced metallic characteristic compared to S, indicating that it has better electronic properties. Nickel diselenide (NiSe₂) is a promising candidate for pseudocapacitors due to its good electrical conductivity for various oxidation states and charge transfer (Gao et al., 2012; Gong et al., 2012). One of the recent trends in electrode preparation for supercapacitors is the direct growth of the active material in current collectors. This method not only eliminates the electrode preparation step but also results in increased specific energy and capacity (Guo et al., 2016).

This study demonstrates the potential of NiSe₂ in supercapacitor applications. Here, Nickel foam and selenium were synthesized by microwave-assisted method. Furthermore, the electrochemical properties of the prepared NiSe₂ cathodes were investigated at three electrodes through a potentiostat/galvanostat system. The electrochemical properties of the prepared NiSe₂ cathodes were investigated in three electrode systems.

2. Materials and Methods

2.1. Materials

Selenium powder, DMF (Dimethylformamide), CTAB (Cetyltrimethylammonium Bromide), and Ammonium solution were used in analytical purity and without additional

purification. All reagents were purchased from Sigma-Aldrich Co. LLC. The reactions were carried out in a specially designed 100 mL Teflon-lined vessel, and heating was performed using a microwave hydrothermal synthesis system called Milestone/FlexiWave Advanced Flexible Microwave Synthesis Platform.

2.2. Methods

0.177 g selenium powder, 0.473 g CTAB, 4.33 mL EDA, 60.63 mL DMF were mixed and ultrasonicated. Then 20 mL of the mixture was placed in teflons. Pre-washed 2x1 cm Nickel foams were added into the Teflon. Teflons were then placed for the microwave process. A microwave irradiation of 900 Watts was applied at 160 °C for 30-45-90 minutes. Afterward, the coated nickel foams were rinsed with deionized water and dried in an oven at 60 °C for 24 hours.

Nickel foam coated with selenium was characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), and Energy dispersive X-ray spectroscopy (EDS). The electrochemical properties of the prepared selenium-coated nickel foams were analyzed using a three-electrode potentiostat/galvanostat system. The supercapacitor properties of the prepared composites were investigated by alternating voltammetry (CV) and galvanostatic charge-discharge (GCD) studies. These electrochemical measurements were performed in 3 M KOH electrolyte medium using a three-electrode potentiostat-galvanostat system. Hg/HgO as reference electrode, counter electrode platinum plate as the working electrode and NiSe₂@Ni-foam as the working electrode was used.

The field specific capacitance (Ca, F cm⁻²) was determined by the following equations calculated:

$$C_a = I \times \Delta t / (S \times \Delta V) \quad (1)$$

3. Results

3.1. X-Ray Diffraction Analysis

XRD spectra of NiSe₂ nanomaterials obtained on nickel foam at different times are given in Figure 1. When the XRD spectra are analyzed, the peaks seen at $2\theta = 45, 52,$ and 76° are thought to belong to nickel foam (Snow crystal-like structure of NiSe₂ as a binder-free electrode for high-performance hybrid supercapacitor). In addition, the peak observed at $2\theta = 33^\circ$ when the synthesis time increased (45 and 90 min), which was not seen at the beginning, was shown to belong to the crystal lattice of the NiSe₂ structure in accordance with the literature (13). The XRD pattern of NiSe₂ fits the standard JCPDS card no 01-075-0610 quite well, showing a hexagonal crystal structure. The reason why other peaks do not appear in the XRD spectrum is thought to be due to the dominant nickel foam peaks suppressing other peaks.

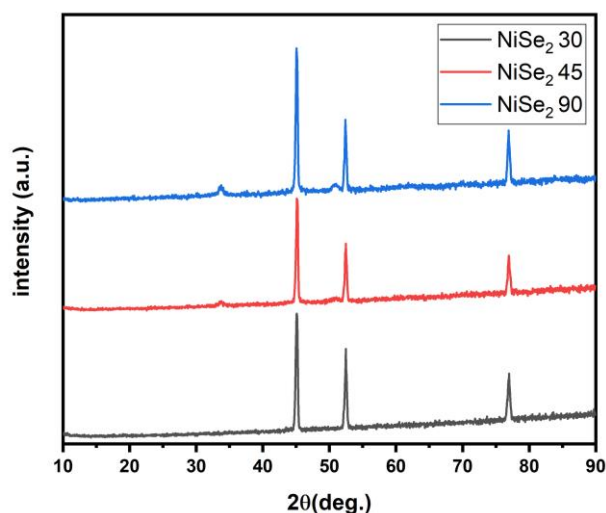


Figure 1. XRD graph of NiSe₂ at 30-45-90 minutes.

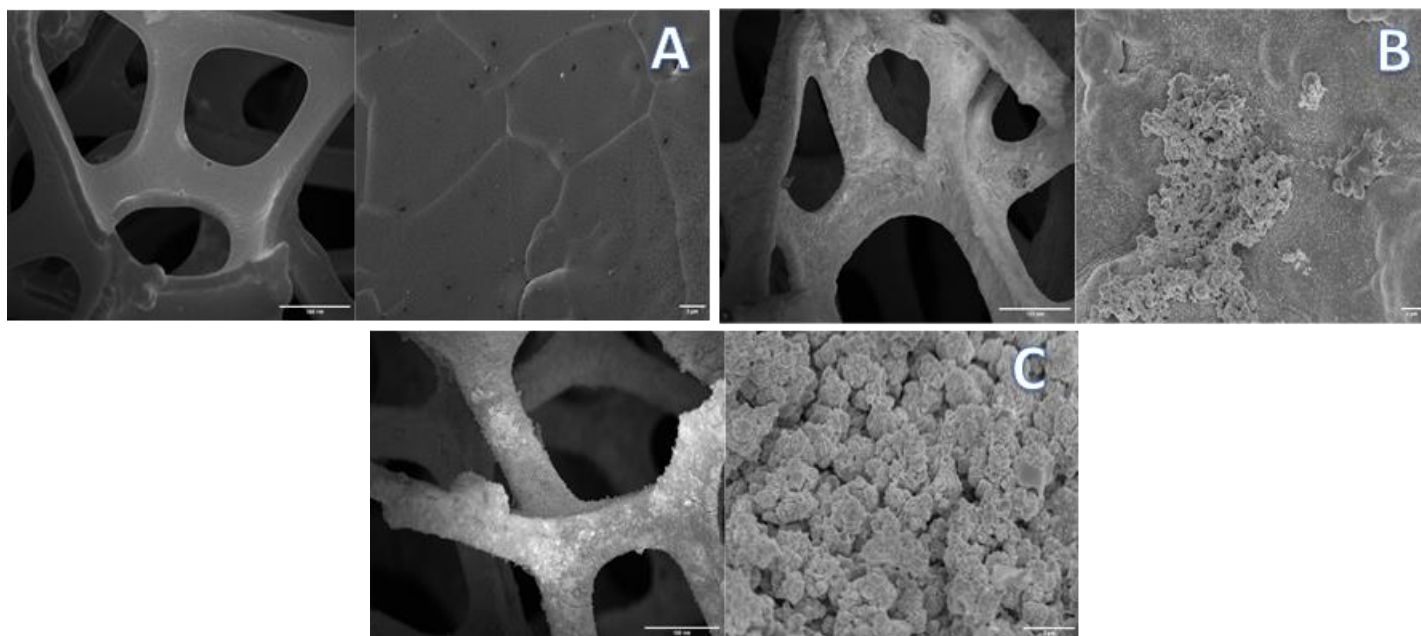


Figure 2. SEM images of NiSe₂ (A) 30 min, (B) 45 min, (C) 90 min.

3.3. Electrochemical Analysis

Figure 3 presents the cyclic voltammetry (CV) curves of NiSe₂ 30 min, NiSe₂ 45 min, and NiSe₂ 90 min nanocomposite as (a), (c), and (e), respectively. Figure 3 includes parts (b), (d), and (f), showing the galvanostatic charge-discharge times for the same materials. The electrochemical properties of NiSe₂ structures grown on nickel foam as an active electrode material for supercapacitor applications were first investigated using CV and GCD experiments in a three-electrode setup containing 3 M KOH aqueous electrolyte. CV curves of NiSe₂ are generated at different reaction times and scan rates ranging from 10 to 100 mV s⁻¹ are shown in Figure 3. As the scanning rate is raised, there is a notable increase in both the area beneath the CV (cyclic voltammetry) curves and the peak current density. Even at a considerably high scanning rate of 100 mV s⁻¹, dual redox

3.2. Microstructure SEM analysis

SEM images show the structures growing on the Nickel foam used to demonstrate the morphology of NiSe₂ (Figure 2). The nickel foam backbone is overlaid with NiSe₂, which is uniformly grown (Figure 2). At higher magnification levels, it can be seen that the particles form a dense morphology with high surface area agglomerates. It is also understood that the particle size of NiSe₂ materials obtained at different times decreases with the effect of time.

peaks remain discernible, indicating a rapid, low-resistance, and reversible redox reaction. Moreover, with the escalation in scan rates from 10 to 100 mV s⁻¹, the oxidation and reduction peaks exhibited a slight shift towards higher and lower potentials, respectively. This outcome could be attributed to the reduced diffusion rate of the hydroxyl group (OH⁻) at elevated scan rates, which might impede the full completion of the electrochemical processes involving the active electrode material. Galvanostatic charge-discharge (GCD) curves were generated at various current levels within the potential range of 0 to 0.45 V (refer to Figure 3). The existence of a flat plateau in the charge-discharge curve (GCD) suggests battery-like behavior in NiSe₂. NiSe₂-45 has significantly higher capacity values than other NiSe₂ samples (NiSe₂-30 and NiSe₂-90). The specific capacity of the NiSe₂-45 structure determined was

3333, 2880, and 2320 F g⁻¹ at current densities of 5, 15, and 20 A g⁻¹, respectively.

The capacity deficit values observed at higher current densities are linked to an electron transfer rate that exceeds the

pace of electrochemical processes. Consequently, the electrode materials are unable to effectively engage in the redox reaction, resulting in a decline in capacity values.

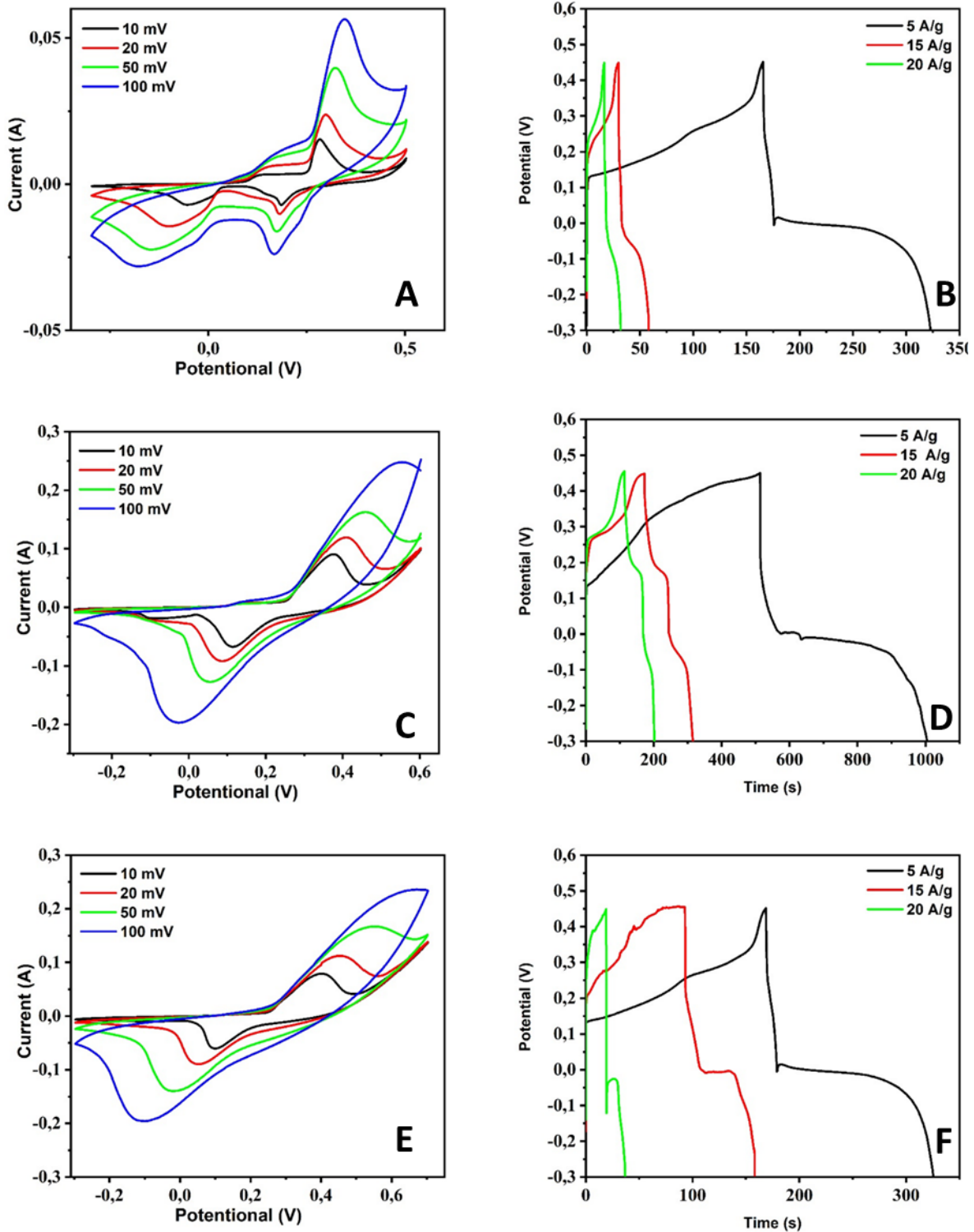


Figure 3. NiSe₂ CV and GCD graphs (A)30 min CV (B)30 min GCD (C) 45 min CV (D)45 min GCD (E)90 min CV (F)90 min GCD.

4. Discussion

XRD spectra of NiSe₂ nanomaterials obtained on nickel foam at different times are given in Figure 1. When the XRD spectra are analyzed, the peaks seen at $2\theta = 45, 52$, and 76° are thought to belong to nickel foam (snow crystal-like structure of NiSe₂ as a binder-free electrode for high-performance hybrid supercapacitor). In addition, the peak observed at $2\theta = 33^\circ$ when the synthesis time increased (45 and 90 min), which was not seen at the beginning, was shown to belong to the crystal lattice of the NiSe₂ structure in accordance with the literature (Bekhit et al., 2022a). These results are in agreement with JCPDS card no 01-075-0610. The reason why other peaks do not appear in the XRD spectrum is thought to be due to the dominant nickel foam peaks suppressing other peaks.

5. Conclusion

The structure of NiSe₂ was synthesized using the direct growth microwave-assisted hydrothermal method using CTAB as a reducing agent. Such a unique morphology provided a sufficient electroactive area for electrochemical reactions, resulting in a high specific capacity of 3333 F g^{-1} at 5 A g^{-1} . This research work indicates that NiSe₂ nanomaterial can be used as electrode material in supercapacitors.

Conflict of Interest

The authors declare that they have no conflict of interest.

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