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In situ X-ray diffraction characterization of $NiSe_2$ as a promising anode material for sodium ion batteries

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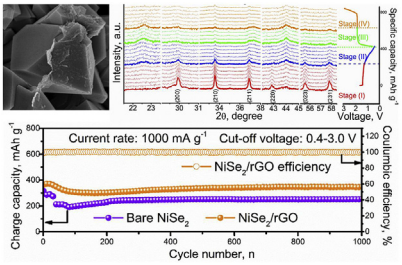
HIGHLIGHTS

- $NiSe_2$/rGO hybrid has been fabricated by a facile one-spot hydrothermal process.
- *In situ* X-ray diffraction analysis reveals the reaction mechanism of $NiSe_2$/rGO.
- The influence of cut-off voltage on electrochemical performance is investigated.
- $NiSe_2$/rGO hybrid exhibits excellent cycling stability for sodium ion batteries.

GRAPHICAL ABSTRACT



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ABSTRACT

Reduced graphene oxide (rGO) homogenously wrapped nickel diselenide ($NiSe_2$/rGO) hybrid has been prepared by a facile one-spot hydrothermal method. When investigated as anode material for sodium ion batteries (SIBs), $NiSe_2$/rGO hybrid delivers a high reversible capacity (433 mAh g^{-1} at 100 mA g^{-1}), superior rate performance (406, 386, 366, 347 and 318 mAh g^{-1} at 200, 500, 1000, 2000 and 5000 mA g^{-1}, respectively) and excellent cycling stability (a capacity retention of 346 mAh g^{-1} after 1000 cycles at 1000 mA g^{-1}) within the 0.4–3.0 V voltage range. *In situ* XRD analysis and *ex situ* SEM/TEM measurement reveal that the high capacity of $NiSe_2$/rGO is originated from the combined Na^+ intercalation and conversion reactions. These results validate the impact of voltage range on electrochemical property, providing a new route to rationalize the limiting factors that affect the performance of $NiSe_2$ anode material. The facile synthesis and superior electrochemical performance of the $NiSe_2$/rGO hybrid render it a promising anode material for SIBs.

1. Introduction

Rechargeable lithium-ion batteries (LIBs) have been extensively employed as the power sources for small consumer electronics, electric vehicles (EVs) and hybrid electric vehicles (HEVs), because of their high safety, environmental friendliness and admirable electrochemical performance [1,2]. However, as lithium resource is unevenly and limited distributed around the world, further development of LIBs is greatly restricted. Recently, sodium-ion batteries (SIBs) have attracted tremendous attentions, and been considered as one of the promising candidates for large-scale energy storage due to the relative abundance resource in the earth crust [3,4]. As

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the intercalation mechanism of Na^+ is similar to that of Li^+, the design and fabrications of SIBs can be adopted from LIBs. Commonly, conventional graphite is used as a standard anode in commercial LIBs on account of its reasonable reversible capacity and optimum potential plateaus. Unfortunately, it is difficult to accommodate and allow Na^+ ions reversible insert/extract into the host graphite, owing to the unfavorable and unstable thermodynamics of graphite intercalation compound with Na^+ [5,6].

In order to satisfy the requirements of high capacity rechargeable SIBs, intensively attempts have been made to investigate possible anode materials with excellent electrochemical performance, such as alloying materials (Sb, Sn) [7–10], metal oxides (NiO, Fe_2O_3) [11–13], and transition metal chalcogenides (TMCs) [14,15]. Recently, owing to intrinsically high conductivity, which can facilitate the migration of Na^+ ion [16,17], TMCs are of great interests and have been considered as promising alternatives to conventional graphite anode for SIBs [18]. Among TMCs materials, the nickel selenide possessed with the unique property, has been widely investigated in various kinds of fields, such as lithium storage [19], hydrogen storage [20] and water splitting [21]. In addition, nickel selenide has also aroused interests for SIBs recently, Zhang et al. [22] reported that the NiSe/C anode demonstrated a reversible sodiation capacity of 280 mAh g^{-1} after 50 cycles. Cho et al. [23] showed that the mixed crystal structures $NiSe_2$ growing on graphene nanosheets exhibited a good performance. Nowadays, main researches have focused on synthesis of the nanostructured $NiSe_2$ with delicate structure design. But further attempts should be conducted to find a facile approach to fabricate nanostructured $NiSe_2$ and improve its electrochemical performance. Moreover, investigating the reaction mechanism and understanding the structural evolution of $NiSe_2$ anode during the long-term sodiation/desodiation process, are still required for high performance SIB synthesis [24–26].

In this study, reduced graphene oxide (rGO) homogenously wrapped nickel diselenide ($NiSe_2$/rGO) hybrid has been fabricated and applied as the anode material of SIBs. It demonstrates a high reversible capacity, enhanced rate capability and excellent cyclic stability. To simplify the synthesis process, a facile one-spot hydrothermal approach has been designed to produce the hierarchical structured $NiSe_2$/rGO hybrid. Moreover, *in situ* X-ray diffraction has been applied to study the reaction mechanism during sodiation/desodiation process, which involves a two-step reversible process. The three-dimensional architecture of $NiSe_2$/rGO hybrid is a promising anode material for SIBs.

2. Experimental section

2.1. Preparation of $NiSe_2$/rGO composite

The $NiSe_2$/rGO hybrid has been synthesized by a facile one-pot hydrothermal method, and the general synthesis process is schematically presented in Fig. 1. The aqueous dispersion of the graphite oxide (GO) was prepared by the oxidization of natural graphite powder using a modified Hummers method. In the typical synthesis process, selenium powder (8 mmol) and NaOH (0.1 mol) were dissolved and dispersed in deionized water (40 mL). Subsequently, $Ni(NO_3)_2 \cdot 6H_2O$ (4 mmol) was dissolved in deionized water (20 mL) and mixed with the EDTA-2Na (2 mmol), then added into the above solution dropwise. Then, 10 mL aqueous GO suspension (5 mg mL^{-1}) solution was mixed and ultrasonically dispersed for 5 h. Subsequently, this as-prepared solution was transferred into a 100 mL Teflon-lined autoclave and heated at 200 °C for 18 h. After cooling down to room temperature naturally, the precipitate was collected by centrifugation and rinsed with deionized water and ethanol for several times, followed by freeze drying to get final product. In comparison, the bare $NiSe_2$ sample was also prepared by a similar synthetic approach without GO suspension.

2.2. Materials characterization

X-ray diffraction (XRD) was performed on a Bruker D8 Advance powder X-ray diffractometer equipped with Cu Kα radiation (λ = 1.5418 Å). For *in situ* XRD experiments, the *in situ* XRD cell was illustrated in Fig. S1A and as reported previously [27]. Thermo gravimetric (TG) analysis of the mixture was conducted on a SDT Q600 TG-DSC apparatus between 25 and 900 °C at a heating rate of 10 °C min^{-1} under air flow. Raman spectra were obtained on the Jobin-Yvon LabRAM HR-800 spectrometer with excitation from an argon ion laser (514.5 nm). X-ray photoelectron spectrometer (XPS) was carried out on a pass energy of 35.75 eV (PHI, PHI5300 system). The microstructure and morphology of products were investigated by the field-emission scanning electron microscopy (FE-SEM) (JEOL, Model JSM-7600F) at an acceleration voltage of 5 kV and a high-resolution transmission electron microscopy (HRTEM, Tecnai G2 F20 S-TWIN, Japan) operating at 200 KV.

2.3. Electrochemical measurements

The electrochemical properties of the anode materials were studied by using CR2025 coin-type cell. The working electrodes were prepared by casting the slurry consisted of active material (bare $NiSe_2$ or $NiSe_2$/rGO) with carbon black and polyvinylidene fluoride in a weight ratio of 7:2:1 on copper foil collector. Then, the electrodes were assembled in an Ar-filled glove boxed using glass fiber as the separator and metallic sodium tablet as reference electrode. The electrolyte was 1.0 M $NaCF_3SO_3$ dissolved in diethylene glycol dimethylether (DEGDME). The galvanostatic charge-discharge profiles were collected at various current densities with cut-off voltages of 0.4–3.0 V and 0.01–3.0 V (versus Na^+/Na) at 25 °C. The active electrode loadings were about 1.0 mg cm^{-2} with a diameter of 14 mm, while the specific capacity (mAh g^{-1}) of electrodes was evaluated based on the total mass of active materials. Cyclic voltammetric (CV) measurements were recorded in the various potential range conducted by a CHI660E electrochemical work-station at a scan rate of 0.1 mV s^{-1}. Electrochemical impedance spectra (EIS) were performed on IM6 (Zahner) electrochemical station by applying an amplified voltage of 5 mV over the frequency range from 100 kHz to 0.01 Hz.

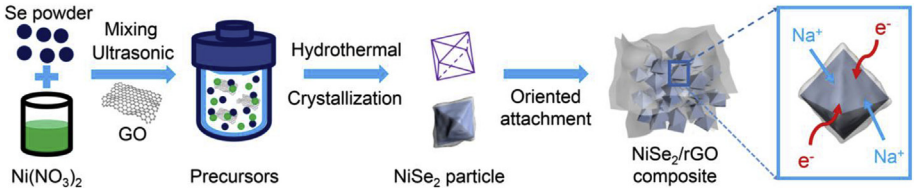

Fig. 1. Schematic illustration of the fabrication procedure of $NiSe_2$/rGO hybrid.