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Facile hydrothermal synthesis of hexapod-like two dimensional dichalcogenide $NiSe_2$ for supercapacitor

Narayanasamy Sabari Arul*, Jeong In Han

Department of Chemical and Biochemical Engineering, Dongguk University, Seoul 04620, South Korea

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ABSTRACT

Hexapod-like two dimensional transition metal dichalcogenide nickel diselenide ($NiSe_2$) structures was synthesized by a facile hydrothermal approach and investigated its electrochemical performance as a supercapacitor electrode for the first time. The obtained material was characterized by XRD, XPS and TEM analysis. The results confirmed the presence of orthorhombic phase of $NiSe_2$ in the synthesized hexapod-like $NiSe_2$ structures. The fabricated $NiSe_2$ electrode on graphite foil exhibited a specific capacitance of 75 F g^{-1} with good cyclic retention of 94% at a current density of 1 mA cm^{-2} after 5000 charge-discharge cycles. Our results indicate that the synthesized hexapod-like $NiSe_2$ structures hold as a promising candidate for the supercapacitor applications.

1. Introduction

Supercapacitor, also known as ultracapacitors, have been recognized as the most promising energy storage device which has fascinated considerable attention due to its high power density, excellent rate capability and cycle life [1]. The electrochemical performance of the supercapacitor is mainly reliant on the electrode material which triggers the research community to develop new electrodes with high energy density, power density and cycle life. Till date, such efforts have been achieved through novel two dimensional (2D) layered materials including graphene, reduced graphene oxides and chalcogenides [2–5]. In particular, 2D transition metal dichalcogenides (TMD) such as NiS_2, CoS_2, MoS_2, VS_2, WS_2 and $MoSe_2$ have been proved as high performance supercapacitor electrode materials [6–11]. However, to the best of our knowledge, reports on 2D TMD hexapod-like $NiSe_2$ as the supercapacitor electrode material has not been reported earlier. In general, $NiSe_2$ can occur in both T and H structures [12]. $NiSe_2$ is a nonmagnetic metal in H structure while it is narrow indirect-band gap (0.1 eV) semiconductor in T structure, which makes it a promising candidate for electronic applications. $NiSe_2$ exhibits unique physical, optical, electrical and electrochemical properties have shown great prospective in a variety of applications such as electrocatalysts for hydrogen evolution reactions, dye sensitized solar cells photoelectrochemical water splitting and rechargeable lithium batteries [13–16]. So far various methods, including pulsed laser deposition [16], hydrothermal [17], solvothermal [18], electrodeposition [19] and solution chemical process [20], have been employed for synthesizing $NiSe_2$ nanostructures. This paper reports the data for facile hydrothermal synthesis of hexapod-like 2D TMD $NiSe_2$ for supercapacitors. The electrochemical performance of hexapod-like $NiSe_2$ was studied using cyclic voltammetry (CV), galvanostatic charge discharge (GCD) and electrochemical impedance spectroscopy (EIS).

2. Experimental

All the reagents used for this synthesis were of analytical grade and used without purification. The synthesis of hexapod-like $NiSe_2$ is as follows. Initially, a required amount of nickel (II) acetate ($Ni(CH_3CO_2)_2.4H_2O$), selenium dioxide (SeO_2) and poly (4-vinylpyridine) were mixed in de-ionized water using a magnetic stirrer for 10 min and the resulting solution was transferred to Teflon-lined stainless steel autoclave containing 35 ml of ethanolamine (C_2H_7NO) and maintained at 180 °C for 15 h. After cooling to room temperature, the obtained products were centrifuged and washed several times with de-ionized water and ethanol and later dried in vacuum oven at 80 °C for 1 h. Finally, hexapod-like $NiSe_2$ structures were obtained by annealing the sample under nitrogen atmosphere in a furnace at 300 °C for 1 h.

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* Corresponding author.
E-mail address: artsabari@gmail.com (N.S. Arul).

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The crystal structure of synthesized hexapod-like NiSe$_2$ was determined by Rigaku Ultima IV diffractometer using CuKα radiation (λ=0.15406 nm, 40 kV, 40 mA) at a scan rate of 4°/min between 20° and 60° (2θ). X-ray photoelectron microscopy (XPS) was performed using a Theta Probe AR-XPS System from Thermo Fisher Scientific with monochromated Al Kα (1486.6 eV) as an X-ray source operating at 15 kV. The transmission electron microscopy (TEM) and field emission transmission electron microscopy (FE-TEM) images were captured using JEM-JEOL 2000EX instrument. The electrochemical measurement was performed using Biologic SP-150 electrochemical workstation using three electrode system in 1 M KOH as the electrolyte under ambient conditions. The hexapod-like NiSe$_2$ (0.5 mg) coated on graphite foil was utilized as working electrode, a platinum wire as a counter, and Hg/HgO as reference electrode, respectively.

3. Results and discussion

Fig. 1a shows the XRD pattern of synthesized hexapod-like NiSe$_2$ electrode material fabricated on graphite foil substrate. The diffraction peaks along (110), (111), (200), (121), (130), (110), (131) and (310) planes can be readily indexed to the orthorhombic structure of NiSe$_2$ (JCPDS no. 18-0886). Furthermore, no other impurity peaks are observed, indicating the structural purity of the synthesized hexapod-like NiSe$_2$. The compositional analysis of hexapod-like NiSe$_2$ was carried out using the XPS analysis and its corresponding survey spectrum is displayed in Fig. 1b. The presence of oxygen and carbon peaks in the spectrum arises due to the interaction with air and the carbon contamination on the surface of the material [21]. The high-resolution XPS spectrum of Ni 2p exhibits binding energy of Ni 2p$_{3/2}$ (853.29 eV) and Ni 2p$_{1/2}$ (870.72 eV), which obviously blue shifted from neutral Ni^0 peaks, as shown in Fig. 1c. The binding energy of Se 3d exhibits a prominent peak S1 at 54.26 eV and a weak peak S2 at 58.61 eV, as displayed in Fig. 1d. The binding energy of S1 reveals a red shift by 1.3 eV from neutral Se^0 (55.6 eV). The weak peak S2 attributes to Se–O bonding structures at the surface [15,19].

Fig. 2a and b shows the TEM images of the hexapod-like NiSe$_2$ micro-structures made up of nanoparticles (~30 nm, Fig. 2c and d) with lattice spacing of 0.382 nm, which matches well with the (110) plane of orthorhombic NiSe$_2$ and are consistent with the XRD results. The possible growth mechanism of hexapod-like NiSe$_2$ micro-structures is shown in Scheme 1. Initially, tiny nuclei were generated in the supersaturated solution and grew into nanoparticles. These nanoparticles were quickly built and spontaneously aggregated into an octahedron like structures. Finally, these octahedron structures were assembled through oriented attachment mechanism for the formation of hexapod-like NiSe$_2$ [22].

The electrochemical performance of hexapod-like NiSe$_2$ electrode material deposited on graphite foil substrate is characterized

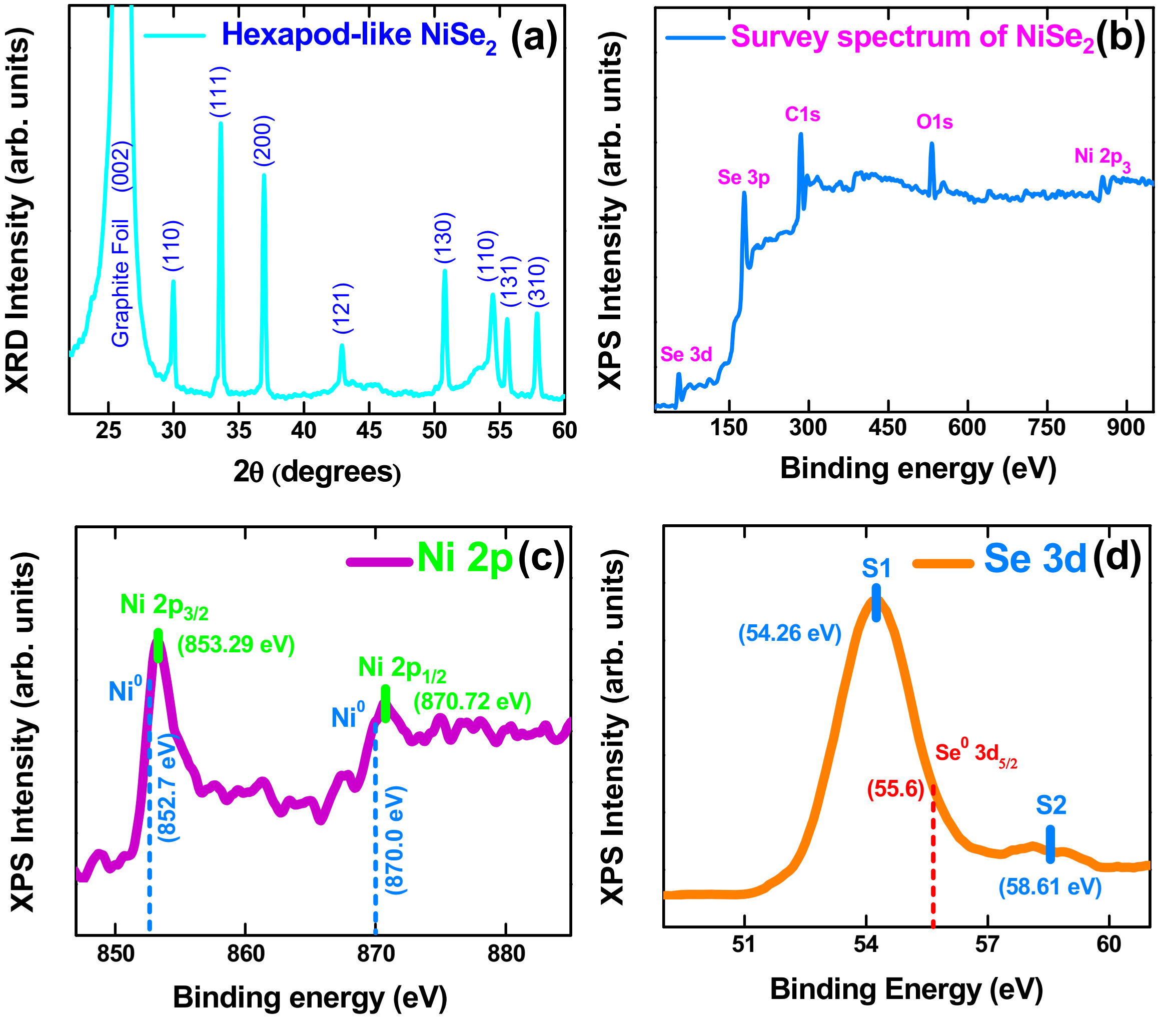

Fig. 1. (a) XRD spectrum; (b) XPS survey spectrum; (c) Ni 2p and (d) Se 3d high-resolution spectra of hexapod-like NiSe$_2$ structures. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)