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Three-dimensional SnS_2 flowers/carbon nanotubes network: Extraordinary rate capacity for sodium-ion battery

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ABSTRACT

Flower-like SnS_2 fabricated by a novel hydrothermal approach are assembled by nano-plates with 1–2 µm in width and 5–10 nm in thickness. Carbon nanotubes are introduced to form a cross-winding network on the surface of SnS_2 nano-plates, which improve the conductivity and Na^+ diffusion of composites. The composites are explored as an anode for sodium-ion battery, and deliver an excellent rate performance. The composites get a reversible capacity of 460 mA h g^{-1} at 20 mA g^{-1} and 180 mA h g^{-1} even increased to 1280 mA g^{-1}, which reveal the importance of carbon nanotubes network to optimize the fast charge-discharge capabilities of SnS_2 flowers.

1. Introduction

Sodium-ion battery (SIB), as a potential substitute for lithium-ion battery (LIB), attracts enormous interest because of its similar electrochemical performance to LIB and high environmental abundance (2.64% of crust reserves) [1]. However, due to the large ionic radius of sodium (1.02 Å) [2], Commercial graphite-based anode are not suitable for SIB. And the feasible anodes are the difficulty needs to be overcome. Various materials, such as carbon, alloy and metal compounds are the optional candidates [3–5]. It is found that materials with layered structure (larger than 3.7 Å layer spacing [1]) have the great electrochemical performances for SIB due to their controllable layer spacing for sodium-ion to insert and move. SnS_2, with a layered CdI_2 crystalline-like structure composed of tin atoms sandwiched between two layers of hexagonal sulfur atoms, in which sodium-ion can easily access the Sn atoms in the layered structure with acceptable volume change [6], is an ideal anode for SIB. To further improve the conductivity and structural stability of SnS_2, Carbon nanotubes (CNTs) are introduced to form a cross-winding network on the surface of SnS_2. The three-dimensional flower assembled by SnS_2 plates and CNTs network provides anode with higher specific surface area, larger tunable free volume and higher conductivity as compared to a planar plate that allows for increased contact area with the electrolyte and more surface sites available for reversible reactions with sodium-ions, and more unblocked and shorter charge transfer and Na^+ diffusion channels. This in turn leads to improved battery kinetics and increased power density while maintaining a small areal footprint and structural stability with reversible volumetric changes [7]. SnS_2/carbon nanotubes (SnS_2/CNTs) show great electrochemical performances and have great potentials for sodium-ion storage.

2. Experimental

Chemicals are all purchased from Sinopharm Chemical Reagent Co., Ltd. $SnCl_4{\cdot}5H_2O$ (7 mL, 0.2 mol L^{-1}) is added into CNTs dispersion (50 mL, 1 g L^{-1}) with stirring for 30 min. Thiourea (2.8 mmol) is added with stirring for 30 min. The resulting dispersion is aged in an autoclave (100 mL) at 180 °C for 700 min. The samples are filtered and washed with distilled water repeatedly. Finally, the products are precipitated by vacuum drying at 60 °C for 6 h (SnS_2 is prepared without CNTs).

The preparation of cell and the equipment models of X-ray diffraction (XRD), Raman Spectrometer, thermogravimetric analysis (TGA), scanning electron microscopy (SEM) and electrochemical measurements are all same as mentioned in literature [8], except for the counter electrode (sodium foil), separator (Whatman GF/D) and electrolyte (1 M $NaClO_4$ dissolved in 100:1 volumetric ratio solution of propylene carbonate and fluorinated ethylene carbonate). And the

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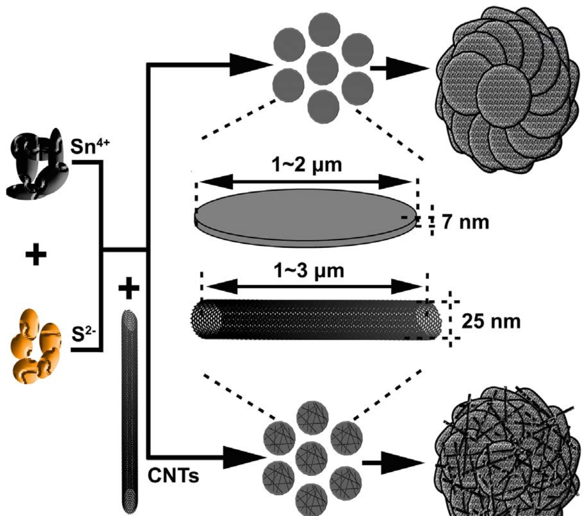

Scheme 1. Mechanism of the formation process of samples.

conductivity is investigated by a four-probe resistivity meter (RTS-9, Guangzhou).

3. Results and discussion

Mechanism of the formation process of samples is shown in Scheme 1. With the stirring, released S^{2-} is absorbed by released Sn^{4+}. Through the hydrothermal reaction, SnS_2 nano-plates are crystallized and assemble into flower-like structure under high-temperature-pressure. And the CNTs form a cross-winding network on the surface of SnS_2 nano-plates via electrostatic interactions..

The structures of samples are confirmed by XRD (Fig. 1a). The as-prepared SnS_2 is indexed to hexagonal phase with P-3m1 space group (PDF No. 23-0677), in which a=b=3.649 Å, c=5.899 Å (lattice parameters). Comparing the XRD patterns between SnS_2 and SnS_2/CNTs, a small peak at ca. 26° is assigned to the CNTs in SnS_2/CNTs. Raman spectra are employed to analyze the component of samples (Fig. 1b, d). The peaks at 211, 308 and 582 cm^{-1} are the first-order E_g mode, A_{1g} mode and the second order effects of SnS_2 phase, respectively [9]. According to the Raman spectrum of CNTs, three intensive peaks at 1340, 1570 and 2687 cm^{-1} are assigned as the fundamental D, G and 2D bands, respectively. The intensity of G band is much higher than D bond, which confirms the great crystalline nature of CNTs [10]. The carbon content presented in SnS_2/CNTs is determined by TGA (Fig. 1c). The mass losses of samples consist of three stages. The initial mass loss from 50 to 250 ℃ is associated with the evaporation of physically adsorbed water and the dopant absolute alcohol [11]. The mass loss between 300 ℃ and 500 ℃ is due to the oxidation of SnS_2 into SnO_2 [12]. And the mass loss in the last region (500–750 ℃) is attributed to the decomposition of CNTs into CO_2 and H_2O [13] (The mass content of CNTs in SnS_2/CNTs is ca. 26.04%)..

SEM shows the morphology of samples. SnS_2 demonstrates typical three-dimensional flower-like structure, which assembled by SnS_2 nano-plates with 1–2 μm in width and 5–10 nm in thickness (Fig. 2a, b). From Fig. 2d, the CNTs have the diameter of 25 nm and the length of 1–3 μm. When CNTs is introduced, they form a cross-winding network coating on the surface of SnS_2 nano-plates (Fig. 2c)..

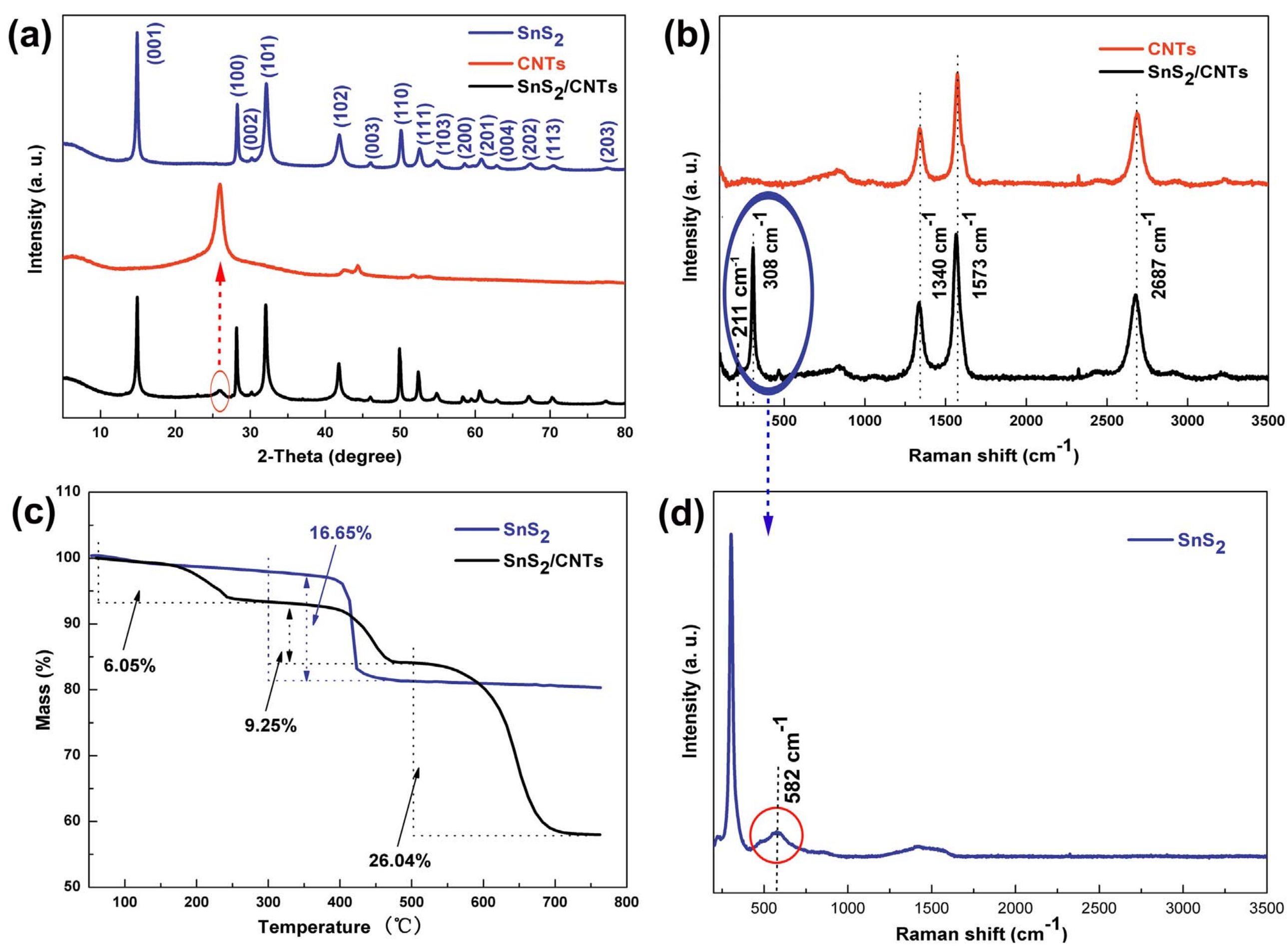

Fig. 1. (a) XRD patterns, (b, d) Raman spectra and (c) TG curves of samples.