

Synthesis of SnO Novel Cabbage Nanostructure and Its Electrochemical Property as an Anode Material for Lithium Ion Battery

Yongkui Cui, Fengping Wang, Hailai Zhao, Muhammad Zubair Iqbal, Ziya Wang, Yan Li, Pengpeng L. V.

Abstract—The novel 3D SnO cabbages self-assembled by nanosheets were successfully synthesized via template-free hydrothermal growth method under facile conditions. The XRD results manifest that the as-prepared SnO is tetragonal phase. The TEM and HRTEM results show that the cabbage nanosheets are polycrystalline structure consisted of considerable single-crystalline nanoparticles. Two typical Raman modes $A_{1g}=210$ and $E_g=112$ cm⁻¹ of SnO are observed by Raman spectroscopy. Moreover, galvanostatic cycling tests has been performed using the SnO cabbages as anode material of lithium ion battery and the electrochemical results suggest that the synthesized SnO cabbage structures are a promising anode material for lithium ion batteries.

Keywords—Hydrothermal process, lithium ion battery, Raman spectroscopy, stannous oxide.

I. INTRODUCTION

NANOSTRUCTURES with controlled morphology and size have attracted considerable attention as the shape and size have a significant influence on their physical-chemical properties [1], [2]. It has been a great challenge to obtain a controllable nanostructure for adapting them to diversified applications.

Binary semiconducting metal oxides are essential nanomaterials because of distinctive properties and are widely used as gas sensors, oxidation catalysts, blue/UV light emitting devices, magnetic sensitive element, transparent electrode, intercalation electrode materials and solar cells [3]-[8]. Among these metal oxides, stannous oxide (SnO), as an important p-type semiconductor, has been intensively investigated. To date various SnO morphologies have been synthesized such as clinopinacoid-type [5], platelets [9], flowers [10], meshes [11], sheets [12], and nanobranchs [13]. Meanwhile, divers methods have been employed to synthesize micro- and nanostructures SnO, such as self-catalytic vapor-liquid-solid (VLS) methods, thermal evaporation and chemical vapor deposition (CVD) [14]-[17]. However, it still remains an uphill task to synthesize SnO novel architectures with a controllable morphology and favorable properties under facile conditions.

Fengping Wang is with University of Science and Technology Beijing, Beijing 100083, PR China (corresponding author, phone: +86-01-6233-2587, Fax: +86-01-6233-2993, e-mail: fpwang@ustb.edu.cn).

Yongkui Cui, Hailai Zhao, Muhammad Zubair Iqbal, Ziya Wang, Yan Li, are with University of Science and Technology Beijing, Beijing 100083, PR China.

Pengpeng LV is with Beijing Key Laboratory of New Energy Materials and Technologies, Beijing 100083, PR China

Development of high energy density rechargeable lithium batteries has been one of the greatest challenges of modern electrochemistry during the last several decades. From a material design point of view, a high performance electrode compound should satisfy several important criteria: a large degree of lithium insertion/extraction (high capacity), high electronic and ionic conductivity, good chemical and structural stabilities (reversibility), and affordable cost. In recent years, microcrystalline powders were employed as electrode materials of lithium ion cell to act as the Li insertion host. In these materials, metal oxides prove to be a promising candidate for its insertion poud can provide high energy density and high cell voltage as high as 5 V versus metallic lithium. Of the various metal oxide material systems, SnO nanostructures are interesting anode materials because of their semiconducting performance combined with high capacity (875 mAhg⁻¹) compared to that of graphite (372 mAhg⁻¹). However, the capacity instability and significant capacity fading with cycling is an important problem specifically with metal oxide based materials due to enormous volume changes during Li alloying and dealloying leading to metal segregation and crystallographic deformation [18], [19]. It has been manifested that the two-dimensional nanodiskettes/sheets may be the most stable and uniform structure under Li ions insertion-extraction cycling [8], [20].

In the present work 3D SnO cabbage-like structures self-assembled with 2D nanosheets were successfully synthesized by using template-free hydrothermal method under facile conditions. The physical and chemical structure of the as-prepared SnO sample was characterized with advance techniques. Moreover, the electrochemical property of the as-prepared SnO cabbages has been studied as an anode material for lithium ion battery.

II. EXPERIMENTAL

A. Synthesis

3D Polycrystalline SnO cabbages self-assembled with nanosheets were fabricated by hydrothermal method using SnCl₂·2H₂O and KOH as the precursors. In a typical synthesis, 10 mL of 1M KOH solution was heated to 90°C under magnetic stirring in a three-neck round bottom flask, and then 50 mL homogeneous solution of 0.5 M SnCl₂ solution was dripped into the KOH solution slowly. Along with the increasing of SnCl₂ solution, the solution changed from transparent to milky white suspension and to pale yellow suspension. Finally the

occurring of dark gray slurry suspension indicates the formation of SnO. Following the completion of reaction, the end product was attained after being washed several times with the de-ionized water and anhydrous ethanol and dried at 60°C for 10 h.

B. Characterization

The phase composition of the product was characterized by X-ray diffraction (XRD, X'Pert MPD) with Cu K α radiation ($\lambda=0.154$ nm). The morphology of the as-prepared sample was examined by field emission scanning electron microscopy (FESEM, ZEISS SUPPER55) and transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) with selected area electron diffraction (SAED) (Tecnai G² F30 S-twin). Raman vibration modes were analyzed under ambient condition by using the Raman spectrometer (Horiba Jobin Yvon Lab RAM HR800) with a 532 nm excitation line. Galvanostatic cycling tests were performed in Swagelok cells assembled under an Ar atmosphere containing O₂ and H₂O at p.p.m. levels in a Mikrouna glove box. The working electrodes were prepared by mixing as-prepared SnO powder as the active material, acetylene black as the conductive agent and polyvinylidene fluoride (PVDF) dissolved in N-methylpyrrolidinone (NMP) as a binder at a weight ratio of 80:10:10. The electrolyte was 1M LiPF₆ in a solvent mixture of ethylene carbonate (EC), methyllethylene carbonate (MEC) and dimethyl carbonate (DMC) (1:1:1 by volume) on a Celgard 2400 polypropylene separator. The galvanostatic cycling tests were performed within a 0.01-1.2 V voltage limit, using a LAND CT2001C battery test system (Wuhan, China).

III. RESULTS AND DISCUSSION

The morphology and structure of the as-synthesized product were examined by FESEM as shown in Fig. 1. Fig. 1 (a) illustrates a representative overview of the sample. It shows the uniform and single dispersed 3D cabbage-like structures with the average size of ~15 μ m at low magnification. The magnified images of an individual cabbage-like structure reveals that, as shown in Fig. 1 (b), the cabbage is self-assembled by crossed and wrinkled nanosheets (called cabbage-leaves) and the thickness of cabbage leaves is ~12 nm in average (in inset of Fig. 1 (b)). This crossed structure forms much larger space and results in high surface to volume ratio.

Further in depth structural characterization of the structure was performed by TEM and HRTEM. Fig. 1 (c) is the TEM image of a cabbage-leaf. Considerable quantities of nanoparticles with the average size of 6 nm are distinctly detected. The lattice fringes in the HRTEM image (Fig. 1(d)) provide the evidence of the single crystalline nature for each nanoparticle. The spacing between adjacent lattice planes is 0.301 nm corresponding to (101) of SnO. The polycrystalline structure of the cabbage-leaf composited with single crystalline nanoparticles is further manifested by the SAED image in the inset of Fig. 1 (d). The novel polycrystalline cabbage-like SnO nanostructure has never been reported previously in the synthesized materials.

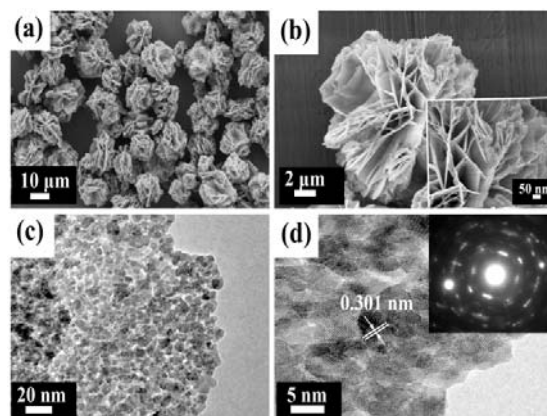


Fig. 1 The typical FESEM images at different magnifications, TEM and HRTEM with the SAED

The phase structure of the as-prepared sample is characterized by XRD and Raman spectroscopy as shown in Fig. 2. Fig. 2 (a) depicts the XRD pattern of the as-synthesized material. All the diffraction peaks are well indexed to the tetragonal structural SnO (JCPDS file No.06-0395 with the lattice constants of $a=b=3.802$ Å, $c=4.836$ Å and $\alpha=\beta=\gamma=90^\circ$). The strong and sharp diffraction peaks indicate good crystallinity, and no any other peak corresponding to other phase has been detected. The lattice parameters of the as-prepared structure were calculated by the equation $1/d^2=h^2/a^2+k^2/a^2+l^2/c^2$ based on the crystal planes of (101), (110) and (002). The attained values $a=b=3.80$ Å, $c=4.84$ Å coincide with the standard values. In addition, further analysis can be attained from Fig. 2 (a), the intensity ratio (0.39) between the (002) and (101) peaks of the as-prepared structure is much higher than the standard value of 0.14 (JCPDS 06-0395), which suggests preferred growth in the as-prepared cabbage-like SnO structures.

Raman spectroscopy was employed to investigate the compositions and chemical states of the sample. The Raman spectrum of the as-prepared SnO, shown in Fig. 2 (b), exhibits two Raman modes at 112 (E_g) and 210 cm^{-1} (A_{1g}), respectively, in good agreement with the theoretical and experimental values of SnO in the literature [21], [22].

Galvanostatic charge–discharge experiments were carried out to evaluate the electrochemical performance of cabbage-like SnO as an anode material for rechargeable lithium ion batteries. The charge–discharge curves of the as-prepared SnO are showed in Fig. 3 (a). In the first galvanostatic delithiation process, a high specific capacity of ~1900 mAhg^{-1} is obtained, which is higher than that of nanoflower structures [15]. In the first lithiation it is 683 mAhg^{-1} which corresponds to about 5 equivalent moles of Li ions per unit mole of SnO. The irreversible capacity of ~1217 mAhg^{-1} in the first cycle was due to the formation of irreversible Li_2O and volume expansion when SnO was transformed to Li_xSn ($0 \leq x \leq 4.4$) alloy in the electrochemical process [8]. There is a plateau in the first discharge curve around 1.0 V, which corresponds to the reported formation of Li_2O and Sn metal [23]. The second discharge and charge capacities are 719 and 669 mAhg^{-1} with a

coulombic efficiency of 93.0 %, as shown in Fig. 3 (c), and this coulombic efficiency increases to 96.5 % for the third discharge-charge capacity, which is greatly superior to the SnO nanoflowers reported [8], [15]. During discharge-charge cycling it shows a well stable performance in the first ten charge-discharge cycles and the discharge capacity, after 25 cycles, remains $\sim 220 \text{ mAhg}^{-1}$ in Fig. 3 (b), which is larger than that of many reported values. The coulombic efficiency remained above 92% for each discharge-charge cycle, except for the first cycle, which is attributed to the formation of irreversible Li_2O .

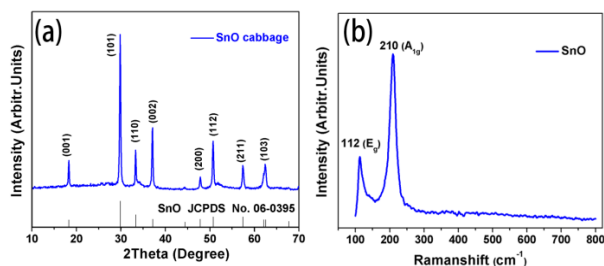
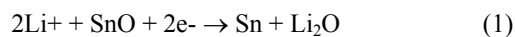


Fig. 2 X-ray diffraction pattern and Raman spectrum at room temperature of as-synthesis SnO

Sn, as a group IV element, displays stoichiometry as high as 4.4 Li/Sn, which makes the first galvanostatic lithiation process a high specific capacity of $\sim 1900 \text{ mAhg}^{-1}$. Moreover, it is possible that the high specific surface area of SnO cabbage-like architectures would effectively enhance its Li storage capacity [24].

The tetragonal SnO is layered structure with Sn-O-Sn layered pyramids that is stacked along the c direction [25]. In the oxide structure, Sn(II) can form the electrochemically active center for Li insertion [26] and SnO layered oxide structure offers higher electrode active specific areas and allows a reversible extraction/insertion of lithium ions from/into the lithium planes, which can result in higher capacities and better rate capabilities. In addition, the interconnected lithium-ion sites between the SnO layers provide fast two-dimensional lithium-ion diffusion, leading to high conductivity of Li.

There are two electrochemical processes in the SnO-based lithium ion batteries:



The discharge-charge process shows good stability and continuous high capacity of $\sim 500\text{-}700 \text{ mAhg}^{-1}$ during the first fifteen cycles, which is superior to the reported results [8]. During Li alloying and dealloying process (2), enormous volume changes will happen for metal oxide based anode materials, resulting to metal segregation and crystallographic deformation [18], which in case of Sn is as high as 200-300% [27], [28]. This reaction can generate a large internal stress, leading to the crack of electrode, loss of electrical contact and large initial irreversible capacity [29]. In this work, the good

stability in discharge-charge cycles for Li-ions battery may be attributed to the cabbage-like structure with more space which help to accommodate the volume changes induced by the lithiation process [19]. In addition, the interlaced structure of SnO can promote the electronic conductivity and the Li_xO phase can enhance the Li-ion migration during Li alloying and dealloying stages as well as prevent further Sn agglomeration [30] on the surface. Nonetheless, the specific capacity still decreased obviously after the fifth cycle due to the volume expansion, resulting in cracking and crumbling which is electrically disconnected from the current collector, and subsequently degenerating of electrode performance during cycling.

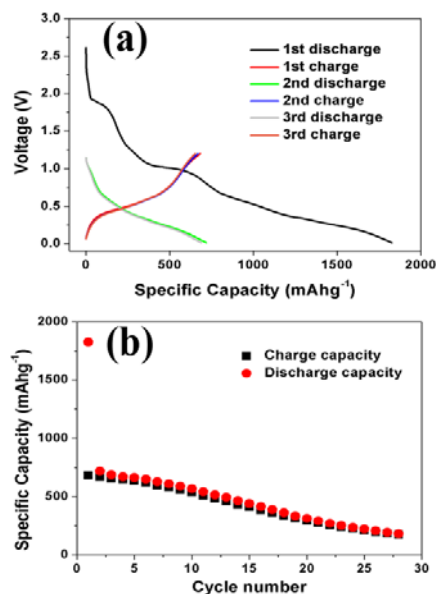


Fig. 3 Charge-discharge profile and cycle performance of as-prepared SnO cabbages

IV. CONCLUSION

The as-synthesized SnO cabbage-like architectures self-assembled by nanosheets have been successfully synthesized using the template-free hydrothermal growth method under facile conditions. The morphology, phase, component and crystal structure were characterized by XRD with EDX, FESEM, TEM, HRTEM with selected area electron diffraction and Raman spectroscopy. The results manifest that the as-prepared SnO is tetragonal phase. The cabbage nanosheets are polycrystalline structure consisted of considerable single crystalline nanoparticles. Two typical Raman modes $A_{1g} = 210$ and $E_g = 112 \text{ cm}^{-1}$ of SnO are observed by Raman spectroscopy. The electrochemical results suggest that synthesized SnO cabbage structure is a promising anode material for lithium ion batteries.

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