

THE SnO₂ NANOTUBE WITH CNT CORE STRUCTURE (SnO₂@VOID@CNT) AND GRAPHENE COMPOSITE ELECTRODE FOR LI-ION BATTERIES

by

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In this study, the problem of volume expansion and agglomeration of SnO₂-based electrode materials has been solved with a unique and multifaced approach. Nanosized SnO₂ is coated around CNT with a void and this structure is decorated between graphene sheets. The problem of aggregation and volume expansion has been solved with nanostructure and voided structure. Besides, conductivity and buffering contributions have been provided by the production composite with graphene and CNT. Herein graphene layers were decorated SnO₂ nanotube with CNT core structure (SnO₂@void@CNT) and used as an anode for Li-ion battery. The electrodes were produced by vacuum filtration technique as flexible and free-standing with no any binder. To compare, pure SnO₂ and SnO₂ decorated graphene/CNT skeleton anodes were prepared and characterized. The SnO₂@void@CNT/graphene anode exhibited excellent cycling performance and rate capability properties.

Key words: tin oxide, CNT, graphene, anode, Li-ion battery

Introduction

The growing global energy demand of the modern world pushes towards more environmentally friendly and more renewable large-scale energy sources in contrast to fossil fuels such as oil, coal and natural gas [1]. The increase in CO₂ emissions and the limited amount of oil also necessitate finding clean energy sources. In this context, electrochemical systems used for energy generation, conversion and storage, including batteries, supercapacitors and fuel cells, play an important role [2]. It is known that especially rechargeable lithium batteries will play a key role in future energy storage systems, including portable electronic circuits (computer, smart phone, etc.) and automotive (electric or hybrid vehicles) applications [3]. The Li-ion batteries have a unique combination of high energy and power density. This feature makes Li-ion batteries a preferred technology for portable electronic circuits, power tools, and electric or hybrid vehicles [4]. Li-ion batteries will significantly reduce CO₂ emissions when electric vehicles replace petrol-powered vehicles. The high energy efficiency of Li-ion batteries enables these batteries to be used in electricity transmission applications used to improve the quality of energy obtained from wind, solar, geothermal and other RES. That is why Li-ion batteries are interesting for both industry and academic studies [5-7].

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Among the electrode materials for Li-ion batteries, tin oxide (SnO₂) is the most promising due to its low cost, environmental friendliness, high theoretic specific capacity (1491 mAh/g), high columbic efficiency, good cycling ability and low operating voltage [8-10]. However, there are some obstacles to the commercial use of SnO₂-based electrode materials: large initial irreversible loss of capacity due to the formation of a thick solid electrolyte interphase during the cycle, volume changes during the charge/discharge process causing pulverization, and small active Sn particles aggregate into larger, inactive Sn clusters during cycling [11-13]. The strategies necessary to solve these existing problems can be grouped under three main headings. Synthesizing various nanostructured tin oxide materials such as SnO₂ nanoparticles, nanowires, and nanospheres can be considered as the first solution proposal [14]. Nanoscale materials provide not only shorter diffusion distances for electrons and ions, but also a buffering effect on volume expansion [15]. Secondly, porous or hollow SnO₂ can be produced. This structure provides sufficient free space to avoid the pulverization problem and can support large volume changes [16]. However, when nanostructured or porous materials tend to aggregate during the cycle, it may not be a perfect solution on its own, especially for long cycles and high speeds. The third effective way to increase the capacity and cycle stability of SnO₂ is to embed SnO₂ into carbon-based materials to form composites [17, 18]. On the one hand, carbon-based materials (CNT, graphene, and amorphous carbon, *etc.*) also significantly increase the conductivity of the electrode. On the other hand, they also act as a buffer to prevent large volume expansion [6].

In this study, versatile solutions have been provided to the difficulties that SnO₂ suffers from as an anode material. The SnO₂ nanoparticles were deposited on the CNT surface by leaving a void space owing to the sacrificial SiO₂, and the SnO₂ nanotube with CNT core structure was obtained. Then, this structure was decorated by compressing it between graphene sheets produced by the Hummer method. The electrode was prepared as flexible and free-standing by vacuum filtration method.

Experimental section

Preparation of SnO₂@void@CNT/graphene composite electrode consists of two separate preliminary stages. First stage is production of graphene oxide from flake graphite by modified Hummer method which is explained and detailed in the Electronic Supplementary Information [19, 20]. Second stage is synthesis of SnO₂@void@CNT structure. Then, graphene oxide and SnO₂@void@CNT are combined together and the electrodes are produced by vacuum filtration as a free-standing and flexible. The production process is shown schematically in the fig. 1.

A typical producing process of SnO₂@void@CNT was as follows: MWCNT (from Array Nano) were oxidized within a mixed H₂SO₄/HNO₃ (3:1 by volume) to activation of the surfaces. The SiO₂ coating of CNT surfaces was carried out by hydrolysis of tetraethyl orthosilicate (TEOS) and polycondensation of SiO₂ reactions in compliance with the Stober method. The 100 mg oxidized MWCNT was dispersed in a mixed solution of 150 ml deionized water and ethanol with an ultrasonic processor for 0.5 hours. The CTAB was added as a surfactant to provide better dispersion and avoid agglomeration of CNT. After ultrasonication, the solution was taken on a magnetic stirrer and approximate 1.5 mL ammonia solution was added until arranged pH range to 10-12 and stirred for another 0.5 hours. Then, TEOS (1.5 mL) and ethanol (15 mL) were mixed in a separate beaker. The TEOS solution was added to this solution dropwise in one hour and was stirred for six hours at room temperature to complete the formation of silica coating. After the process, SiO₂@CNT was collected by vacuum

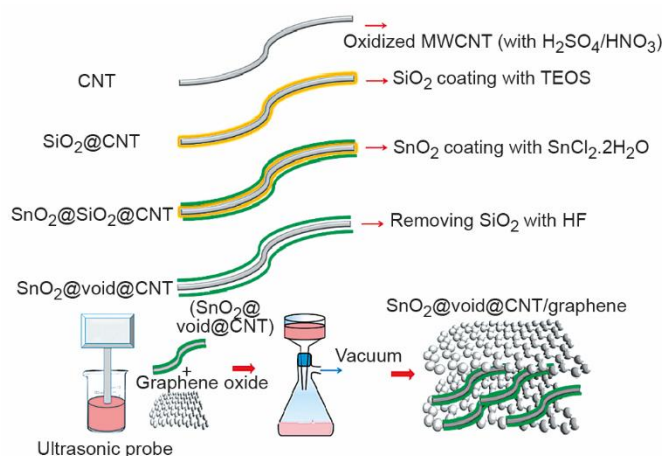


Figure 1. Schematic illustration of production and structure of SnO₂@void@CNT/graphene composite electrode

filtration, washed with ethanol and water and dried at 80 °C for 12 hours. The SnO₂@SiO₂@CNT was fabricated by a facile solvothermal method. Typically, 100 mg of SiO₂@CNT and CTAB were dispersed in 100 mL distilled water and ultrasonically treated for 30 minutes and 0.112 g of SnCl₄, 0.30 g of urea, acidic acid were added to the solution under magnetic stirring for one hour. The final product was obtained by vacuum filtration by washing with water several times. After being dried at 80 °C for 12 hours, SnO₂@SiO₂@CNT was obtained. Subsequently, SnO₂@SiO₂@CNT was selectively etched in 3% HF solution for 15 minutes to discard sacrificial SiO₂ layer to fabricate SnO₂@void@CNT structure. The etching process was performed slowly and precisely at a relatively low HF concentration. The obtained product was washed with water several times until a pH value of 6 was achieved and dried at 80 °C for 12 hours.

In order to prepare SnO₂@void@CNT/graphene composite electrode, graphene oxide, SnO₂@void@CNT structure and CTAB were co-dispersed in 100 mL de-ionized water for 30 minutes. The 5 mL hydrazine hydrate solution was directly added to reduce graphene oxide to graphene and sonication was carried on for an additional 15 minutes. The mixture was then vacuum filtered using PTFE filter paper (Millipore) with the pore size of 220 nm. Finally, the obtained free standing and flexible SnO₂@void@CNT/graphene electrode was dried at 80 °C and peeled off from filter paper. Since the filter paper had a diameter of 47 mm, the produced electrodes had to be cut into diameters suitable for the CR2016 cell. To make this more practical, a mold with the electrode diameter holes was placed on the filter paper and 3 electrodes could be produced at once. For compare, two more anodes were prepared as SnO₂ and SnO₂/CNT/graphene composite. Pure SnO₂ was synthesized with using SnCl₄ and SnO₂ anode was produced with the conventional slurry method. To produce free-standing and flexible SnO₂/CNT/graphene composite anode, pure SnO₂ powders were decorated CNT and graphene skeleton system by using the ultrasonic process and vacuum filtered through filter paper. Details of the preparing processes for these two electrodes are presented in the Electronic Supplementary Information

The X-ray diffraction patterns of the samples were recorded on a RIGAKU D/MAX 2000 X-ray diffractometer with Cu K α radiation during a scan range of 5°-90° at a scan rate of 10° per minute. The morphologies of the samples were observed by a SEM (FEG SEM,

JEOL 6335F) transmission electron microscopy (TEM, Jeol JEM2100F). The thermogravimetric analysis was conducted using a thermal gravimetric analyzer (a NETZSCH DTA-TG, heating rate: 10 °C per minute, atmosphere: air) to determine weights of SnO₂ and carbon in composite anode.

Electrochemical properties were evaluated by using CR2016 half cells assembled in argon filled glove box. In the half cells, the free standing and flexible electrode, Li foil, a polypropylene (PP) film (Cellgard 2300) and 1 M lithium hexafluorophosphate (LiPF₆) solution in EC:DMC (1:1 by vol) were used as anode, cathode, separator and electrolyte, respectively. Charge-discharge tests were carried on a MTI BST8-MA Battery Analyzer with the potential range of 0.01-2.5 V at a constant current density of 200 mA/g. Cyclic voltammetry (0.01-3 V) was detected on a Gamry Instrument Version 5.67 at 0.2 mV/s. Electrochemical impedance spectroscopy (EIS) measurements were conducted on the same work station with the frequency range of 100 kHz-0.01 Hz.

Results

To produce SnO₂ nanotube with CNT core structure (SnO₂@void@CNT), the first stage is SiO₂ coating of CNT surface. Figure 2(a) shows an SEM image of SiO₂@CNT and we can see that CNT surfaces were smoothly coated with SiO₂ by hydrolysis of TEOS. For comparison, SEM image of acid-treated pure CNT is presented in fig. S1 and change of CNT before and after coating is clearly seen [21]. Second step is depositing SnO₂ crystals onto SiO₂@CNT structure. When coated with SnO₂, the smoothness of the SiO₂@CNT surface is disappeared and the diameter of the tubes is increased as can be seen in fig. 2(b). Last step is slight and slow etching of SnO₂@SiO₂@CNT structure with 3% HF solution. Figure 2(c) shows SnO₂@void@CNT structure after etching and removing SiO₂. The TEM analysis was used for further confirmation and detailed visual information of the structure, fig. 2(d). Having a void between the tube and SnO₂ and placing this structure between graphene layers have been provided to the volume expansion problems of SnO₂ during the cycling. Similar to the advantages of yolk-shell morphology, SnO₂@void@CNT/graphene composite can provide the adequate free space for alleviating the volume variation and accommodating the stress during lithiation.

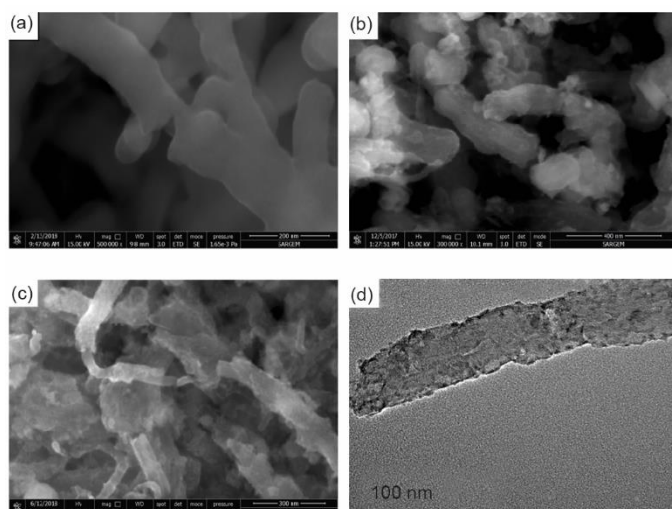


Figure 2. The SEM image of
(a) SiO₂@CNT,
(b) SiO₂@SnO₂@CNT,
(c) SnO₂@void@CNT, (d) TEM
image of SnO₂@void@CNT

During electrode production process, XRD analysis was employed to the samples after for each of the three steps. In addition, XRD results for pure SnO₂, bare CNT, graphite and graphene oxide are also given in the figs. S1 and S4. Figure 3 presents XRD patterns of SiO₂@CNT, SnO₂@SiO₂@CNT and SnO₂@void@CNT/graphene composite electrodes. Considering of patterns of SiO₂@CNT (line 1) in fig. 3, it can be seen that a sharp diffraction peak is located at 26° which can be well indexed to CNT (JCPDS No. 00-026-1076) [22, 23].

Additionally, there is a broad diffraction peak located at around 20° indicating that amorphous SiO₂ phase [24, 25]. After SnO₂ depositing of SiO₂@CNT, the XRD pattern is seen as a line 2. Besides the CNT and amorphous SiO₂ peaks, the characteristic peaks of SnO₂ (JCPDS No.00-041-1445) are also clearly seen in the XRD pattern of SnO₂@SiO₂@CNT. It should be noted that the main peak of SnO₂ at 26° overlapped with the peak of CNT at 26° [26]. The SnO₂@void@CNT structure obtained after etching process of SnO₂@SiO₂@CNT was combined with graphene and electrodes were prepared by vacuum filtration. The upper pattern (line 3) shows SnO₂@void@CNT/graphene composite structure and contains SnO₂, CNT and graphene peaks. Besides the prominent SnO₂ peaks and the overlapped CNT peak, there is also a broad peak of 23°, corresponding to the (002) plane of the graphene [18]. No other peaks indicate the absence of impurities or residual SiO₂.

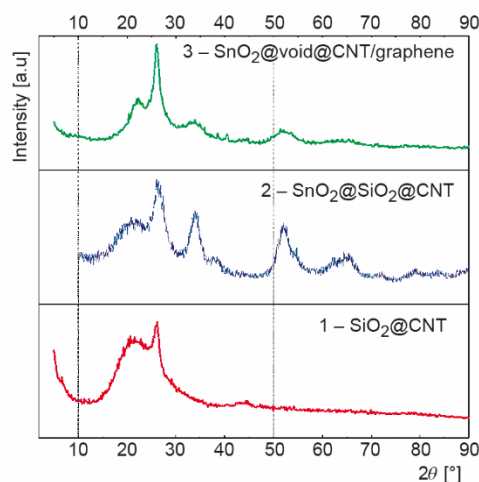


Figure 3. The XRD patterns of 1 – SiO₂@CNT, 2 – SnO₂@SiO₂@CNT and 3 – SnO₂@void@CNT/graphene

To compare the performance of SnO₂@void@CNT/graphene composite electrodes, two more types of electrodes were produced. The first is pure SnO₂ powders, SEM image and XRD pattern of which are given in fig. S4. The second one is the SnO₂/CNT/graphene electrode, which was produced as a free standing and flexible electrode by vacuum filtration method after bringing together the SnO₂ with graphene and CNT with ultrasonic processor. Figure 4(a) presents cross-sectional SEM image of SnO₂@void@CNT/graphene composite electrode. As can be seen from the image, SnO₂@void@CNT was distributed between graphene layers. Figure 4(b) displays cross-sectional SEM image of SnO₂/CNT/graphene and proves that the SnO₂ structure is placed homogeneously between the graphene sheets and the CNT. In addition to the cross-sectional images, EDS analyzes were also performed to show the SnO₂ present in the structure, figs. 4(d) and 4(e).

Figure 4(c) presents optical image of the electrodes. The free-standing electrodes were smoothly peeled off the membrane after drying at the oven. The electrodes with an average thickness of 40 μm can be easily bent like a piece of paper without any damage. In order to find the weight percentage of the SnO₂ for two electrodes, TG analyses were carried out, fig. 4(e). The weight losses before 200 °C are due to adsorbed water molecules or other small molecules. The sharp decrease in the range of 200 °C-650 °C can be explained as the combustion of carbon [27]. The SnO₂ content of the electrodes was calculated based on the mass

losses in this 200-650 °C range and determined to be 34% and 29% for SnO₂/CNT/graphene and SnO₂@void@CNT/graphene electrodes, respectively.

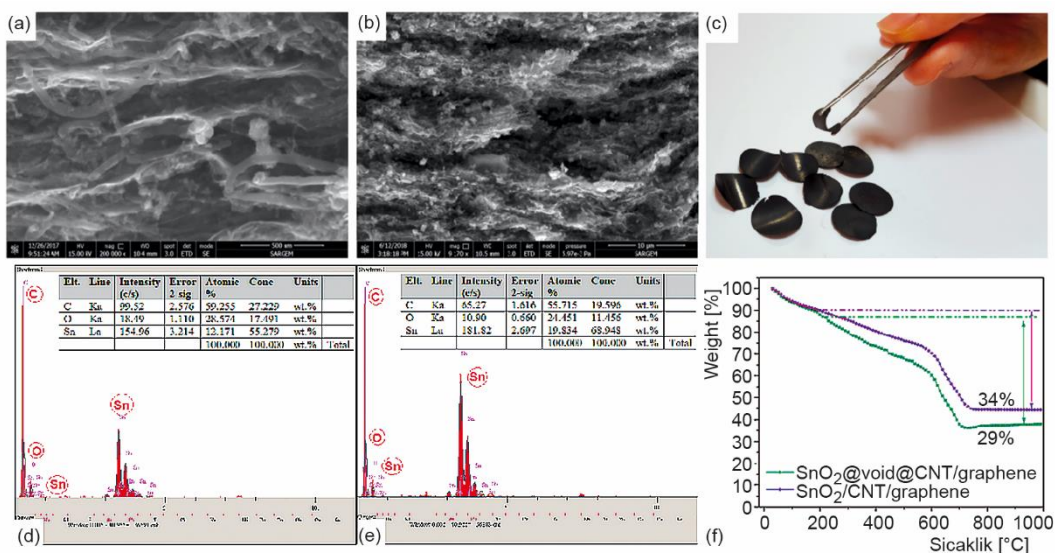


Figure 4. Cross-sectional SEM image of (a) SnO₂@void@CNT/graphene, (b) SnO₂/CNT/graphene, (c) photograph of the electrodes, EDS spectrum of (d) SnO₂@void@CNT/graphene, (e) SnO₂/CNT/graphene, and (f) TG results of the electrodes

The electrochemical properties of the SnO₂@void@CNT/graphene composite, which was produced as a solution to the problem that SnO₂ suffers as an anode material, were investigated by preparing a coin-type battery. Free-standing SnO₂@void@CNT/graphene composite electrode was directly used as a working electrode without any conductive additives or binder. Figure 5(a) presents cyclic voltammetry (CV) curves for initial five cycles between 0.01 V-3 V (*vs.* Li/Li⁺). A reduction peak is observed in the first cycle at 0.57 V, indicating the formation of solid electrolyte interface (SEI) layer, eq. (1) as well as decomposition of SnO₂ to amorphous Li₂O and metallic Sn, eq. (2) [28]. In the first cathodic scan, the peak at 0.57 V is ascribed to the formation of Li_xSn, eq. (3) [29]. The peak of this reaction is seen at 0.63 V for subsequent cycles. The slope of 0.01-0.28 can be attributed to Li_xC formed by the induced of Li into the carbon, eq. (3) [30]. An oxidation peak is observed at 2.4 V, indicating a partially reversible Sn to SnO₂ reaction [31].

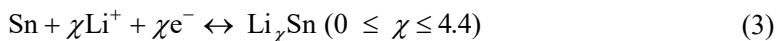
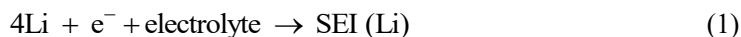


Figure 5(b) indicates charge/discharge profiles of free-standing SnO₂@void@CNT/graphene composite electrode on the selected cycles. The voltage plateaus detected in the charge and discharge curves agreeing to the oxidation/reduction peaks in the CV curves can be attributed to lithium ion insertion and de-insertion reactions. The SnO₂@void@CNT/graphene composite electrode shows specific capacity of 1197 mAh/g and 860 mAh/g for first discharge and charge, respectively. At the second cycle, the electrode exhibited 902 mAh/g and 777 mAh/g of discharge and charge capacity values. The loss of capacity after the first cycle is due to SEI film formation and damage of the structure suffering volumetric expansion [32]. Besides, coulomb efficiencies of the electrode are 71%, 86%, 97%, 96%, and 93% for 1st, 2nd, 5th, 100th, and 400th cycles, respectively.

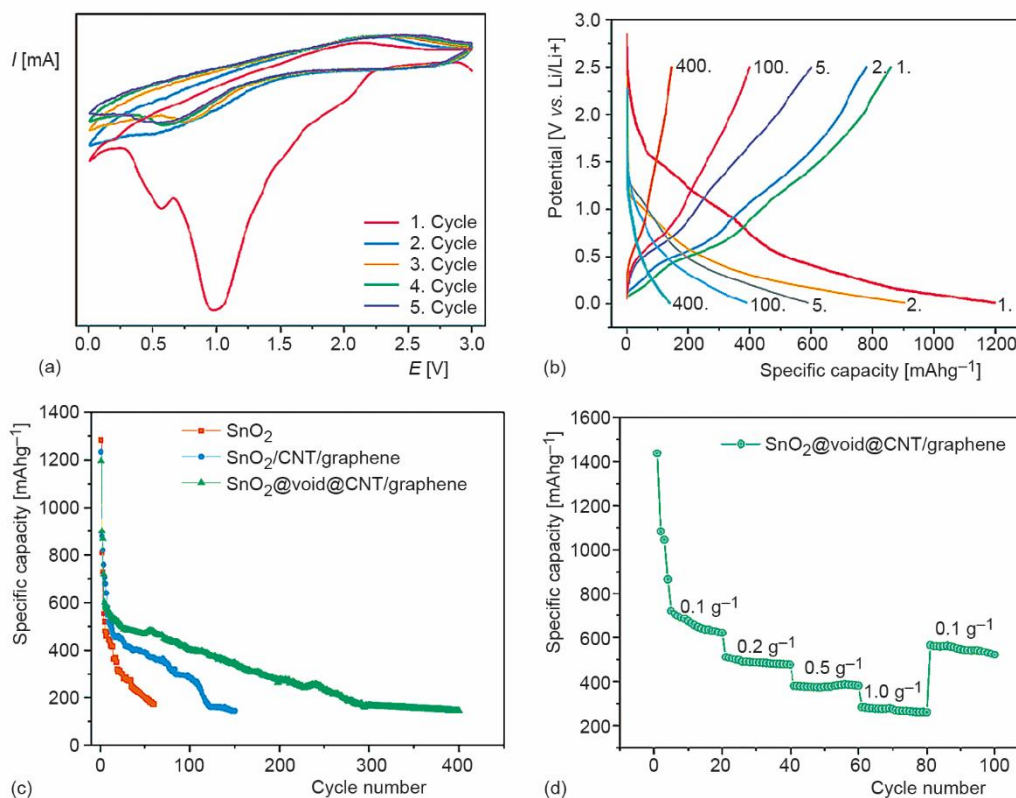


Figure 5. (a) The CV curves, (b) charge/discharge profiles of SnO₂@void@CNT/graphene electrode, (c) cycling performance of three electrodes, and (d) rate capabilities of SnO₂@void@CNT/graphene electrode (for color image see journal web site)

To compare the electrochemical performance of the SnO₂@void@CNT/graphene electrode, two different types of anodes were produced. An electrode was prepared with the traditional slurry method onto copper foil from pure SnO₂ powders. In addition, a free-standing and flexible electrode was made from pure SnO₂ powder, graphene and CNT named as SnO₂/CNT/graphene. Figure 5(c) presents the cycling performance of SnO₂@void@CNT/graphene, SnO₂/CNT/graphene and SnO₂ electrodes. The SnO₂ electrode shows the highest specific discharge capacity but after second cycle a sudden decrease is observed in capacity val-

ues. The rapid capacity drop in the first cycles is due to the formation of Li₂O and SEI on the electrode surface [33]. At the 60th cycle, the battery has reached the end of its life. The drastic volume expansion that occurred during the insertion/extraction of the lithium ions caused the electrode to pulverization and made it unusable. As a solution to the problem that SnO₂ suffers as an anode material, SnO₂ powder is placed in a skeleton consisting of graphene and CNT. The SnO₂/CNT/graphene electrode exhibited a relatively stable state up to 100 cycles, although a decrease in the capacitance value was observed in the first 20 cycles. The CNT/graphene skeleton structure showed a buffering effect against volume expansion of SnO₂. Volume expansion is not the only problem with SnO₂ during alloying/dealloying process. Besides, SnO₂ particles tend to aggregate into severe Sn clusters during cycling [34]. In the SnO₂/CNT/graphene electrode, combining graphene, CNT, and SnO₂ separately may not have fully achieved the uniform distribution of SnO₂ and did not help overcome the agglomeration problem. The SnO₂@void@CNT/graphene electrode performed the best cycling performance because solutions with different perspectives have been provided to the problems that SnO₂ suffers. The SnO₂ nanotube with CNT core structure can alleviate huge volume expansion by providing void space [35]. In addition, since the structure is sandwiched between graphene layers, it is supported by a carbon-based structure both from the inside and the top. Moreover, homogeneous and nanostructured SnO₂ nucleated on CNT can shorten the diffusion distance during the cycle and prevents aggregation and pulverization [13, 36, 37]. The SnO₂@void@CNT/graphene electrode also showed remarkable rate performance in the afterwards rate test. The discharge capacities were about 400 mAh/g and 300 mAh/g when discharged at 0.5 1/Ag and 1.0 1/Ag, respectively. This performance under high current density can be attributed to fast load transfer and stable structure [38]. The electrode still shows capacity of 600 mAh/g after 100 cycles.

Conclusion

In summary, graphene layers were decorated with SnO₂ nanotube with CNT core structure (SnO₂@void@CNT) and prepared free-standing and flexible anodes for Li-ion batteries. According to structural and morphological test results, creating a void space between CNT and SnO₂ by using sacrificial SiO₂ layer, homogeneously covering the surface with SnO₂, and decoration between graphene layers were successfully carried out. In addition to this electrode, two more electrodes, pure SnO₂ and SnO₂/CNT/graphene, were produced their electrochemical properties were compared. The solution proposals applied to improve the disadvantageous electrochemical performance of SnO₂ show themselves in the battery test results. The SnO₂@void@CNT/graphene electrode exhibited a significant performance improvement in terms of capacity and rate capability.

Acknowledgment

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Electronic supplementary information

Graphene oxide production

In this study, the modified Hummer method was used for the production of graphene oxide. As a starting material, 3 g of graphite flakes were mixed in 112.5 mL H₂SO₄ and 37.5 mL HNO₃ solution for 2 hours, then washed with distilled water and dried. Then, 1 g of

graphite was subjected to heat treatment at 800 °C for 120 seconds. The thermally treated graphite was then stirred in 0.5 g of NaNO₃ and 23 mL of H₂SO₄ for about two hours. The beaker was placed in an ice bath, the temperature of which could be reduced to -20 °C. The 3 g of KMnO₄ was added carefully and mixing was continued for 30 minutes. It was then stirred at room temperature for 30 minutes. Distilled water was added to the mixture and the temperature was brought to 98 °C, and mixing was continued here. The 150 mL of distilled water and 3% H₂O₂ are added and mixed for another 2 hours and the mixture turns green. The solution obtained will be washed with 100 mL of 30% HCl solution per gram after filtering. Afterwards, it was washed with distilled water until the pH was 6-6.5 and filtered. The product obtained is called graphene oxide. Figure S1 shows XRD patterns of flake graphite and graphene oxide. Figure S2 displays Raman spectrum of graphene oxide and graphene/CNT. Figure S3 presents SEM image of bare CNT, flake graphite and graphene oxide.

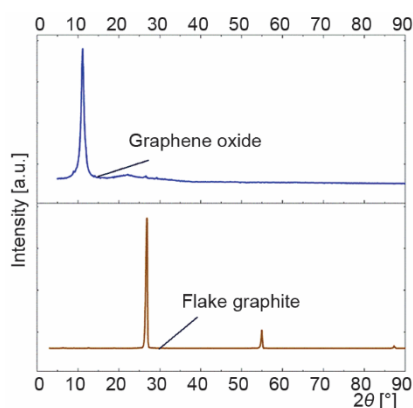


Figure S1. The XRD patterns of flake graphite and graphene oxide

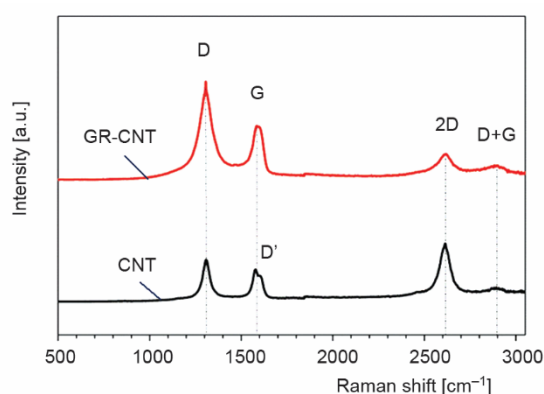


Figure S2. Raman spectrum of graphene oxide and graphene/CNT

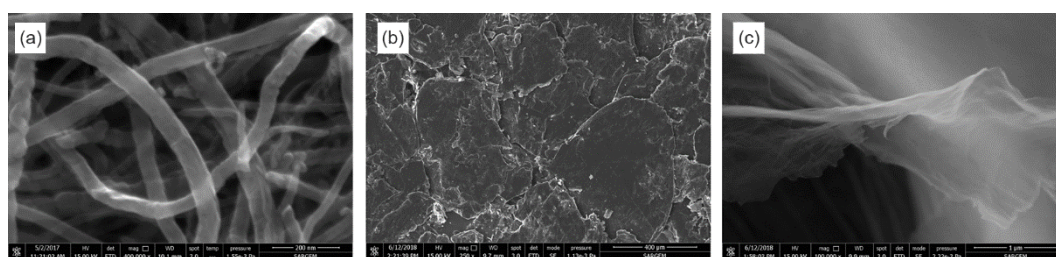


Figure S3. The SEM image of (a) bare CNT, (b) flake graphite and (c) graphene oxide

Production of pure SnO₂

The 2.25 g SnCl₂ and 100 mL distilled water were mixed using a magnetic stirrer for 0.5 hours. Then, the NaOH solution was slowly added into the solution until the pH value reached 13 in order to make a white precipitation and continuously stirred for another 0.5 hours. Resulting white product was washed several times in a centrifuge and dried at 80 °C for 24 hours. Figure S4 shows SEM image of SnO₂ and XRD pattern of SnO₂.

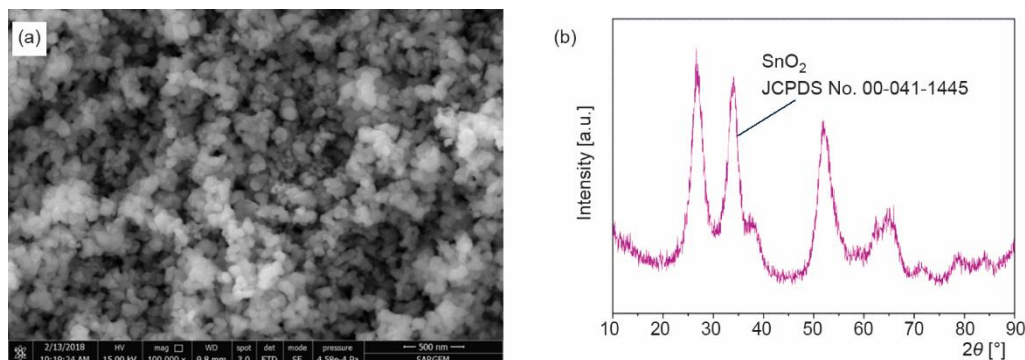


Figure S4. (a) The SEM image and (b) XRD pattern of SnO₂

Production of SnO₂ and SnO₂/CNT/graphene electrodes

Pure SnO₂ electrode was prepared by the traditional slurry method. The SnO₂ powders were added to the slurry in a weight ratio of 80% as active material. By adding 10% conductive material (carbon black) and 10% binder (PVDF dissolved in NMP solution), it was plastered on the copper foil with the dr blade technique.

To prepare SnO₂/CNT/graphene electrode, graphene oxide and CNT were dispersed in 100 mL distilled water by using ultrasonic probe. The CTAB as a surfactant was added to solution. After 30 minutes of sonication, SnO₂ powders were added and ultrasonically treated for additional 15 minutes. Then 5 mL hydrazine hydrate solution was directly added to reduce graphene oxide to graphene and sonication was carried on for an additional 15 minutes. The mixture was then vacuum filtered using PTFE filter paper (Millipore) and peeled off after drying.

References

- [1] Wen, Y., *et al.*, Heteroatom-Doped Graphene for Electrochemical Energy Storage, *Chinese Sci. Bull.*, 59, (2014), 18, pp. 2102-2121
- [2] Li, Z., *et al.*, Particulate Modification of Lithium-Ion Battery Anode Materials and Electrolytes, *Particuology*, 83, (2023), Dec., pp. 129-141
- [3] Mand Khan, B., *et al.*, Role of Graphene-Based Nanocomposites as Anode Material for Lithium-Ion Batteries, *Mater. Sci. Eng. B Solid-State Mater. Adv. Technol.*, 287 (2021), Sept., 116141
- [4] Ullah, K., *et al.*, Recent Trends in Graphene Based Transition Metal Oxides as Anode Materials for Rechargeable Lithium-Ion Batteries, *Nano Trends*, 1 (2022), Nov., 100004
- [5] Nzereogu, P. U., *et al.*, Anode Materials for Lithium-Ion Batteries: A Review, *Appl. Surf. Sci. Adv.*, 9 (2022), Mar., 100233
- [6] Yuan, S., *et al.*, Carbon-Based Materials as Anode Materials for Lithium-Ion Batteries and Lithium-Ion Capacitors: A Review, *J. Energy Storage*, 61 (2022), Dec., 106716
- [7] Li, X., *et al.*, Recent Progress in the Carbon-Based Frameworks for High Specific Capacity Anodes/Cathode in Lithium/Sodium Ion Batteries, *Xinxing Tan Cailiao/New Carbon Mater.*, 36 (2021), 1, pp. 106-116
- [8] Deng, X., *et al.*, SnO₂-MoO₃ Nanoparticles Anchored in Carbon Nanotubes as a Large-Capacity, High-Rate, and Long-Lifetime Anode for Lithium-Ion Batteries, *Ceram. Int.*, 47 (2021), 19, pp. 27022-27031
- [9] Li, Y., *et al.*, A Nanoscale Interlayer Void Design Enabling High-Performance SnO₂-Carbon Anodes, *Carbon N. Y.*, 183 (2021), Oct., pp. 486-494
- [10] Fan, B., *et al.*, A Facile Strategy Towards High Capacity and Stable Sn Anodes for Li-Ion Battery: Dual-Confinement via Sn@SnO₂ Core-Shell Nanoparticles Embedded in 3D Graphitized Porous Carbon Network, *J. Alloys Compd.*, 857 (2021), Mar., 157920

- [11] Wang, X., *et al.*, Electrospun Layers by Layers Orderly Stacked SnO₂@aligned Carbon Nanofibers as High Conductivity, Long Cycle Life Self-Standing Anode for Reversible Lithium Ions Batteries, *Surfaces and Interfaces*, 29 (2022), Feb., 101814
- [12] Premasudha, M., *et al.*, Hydrothermal Synthesis and Electrochemical Behaviour of SnO₂/C@rGO as an Anode Material for Na-Ion Batteries, *Chem. Phys. Lett.*, 805 (2022), Feb., 139970
- [13] Wei, L., *et al.*, A Facile Assembly of SnO₂ Nanoparticles and Moderately Exfoliated Graphite for Advanced Lithium-Ion Battery Anode, *Electrochim. Acta*, 432 (2022), June, 141210
- [14] Wei, L., *et al.*, SnO₂/Sn Particles Anchored in Moderately Exfoliated Graphite as the Anode of Lithium-Ion Battery, *Electrochim. Acta*, 442 (2022), Dec., 141908
- [15] Yang, L., *et al.*, SnO₂ Nanoparticles Compositing with Biomass N-Doped Carbon Microspheres as Low Cost, Environmentally Friendly and High-Performance Anode Material for Sodium-Ion and Lithium-Ion Batteries, *J. Power Sources*, 547 (2022), Sept., pp. 1-11
- [16] Xin, Y., *et al.*, Engineering Amorphous SnO₂ Nanoparticles Integrated Into Porous N-Doped Carbon Matrix as High-Performance Anode for Lithium-Ion Batteries, *J. Colloid Interface Sci.*, 639 (2023), June, pp. 133-144
- [17] Li, W. L., *et al.*, Heterojunction of SnO₂/Sn Nanoparticles Coated by Graphene-Like Porous Carbon as Ultrahigh Capacity Anode of Lithium-Ion Batteries, *J. Alloys Compd.*, 948 (2023), July, 169811
- [18] Zhou, F. Y., *et al.*, Porous SnO₂ Nanospheres Coated with Reduced Graphene Oxide for Formaldehyde Gas Sensor: Synthesis, Performance and Mechanism, *J. Mater. Res.*, 38 (2023), Jan., pp. 1266-1281
- [19] Marcano, D. C., *et al.*, Improved Synthesis of Graphene Oxide, *ACS Nano*, 4 (2010), 8, pp. 4806-4814
- [20] Alaf, M., *et al.*, Graphene Supported Heterogeneous Catalysts for Li-O₂ Batteries, *Appl. Surf. Sci.*, 380 (2016), Sept., pp. 185-192
- [21] Zhang, M., *et al.*, Fabrication of Mesoporous Silica-Coated CNT and Application in Size-Selective Protein Separation, *J. Mater. Chem.*, 20 (2010), 28, pp. 5835-5842
- [22] Alaf, M., *et al.*, Double Phase Tin oxide/tin/MWCNT Nanocomposite Negative Electrodes for Lithium Microbatteries, *Microelectron. Eng.*, 126 (2014), Aug., pp. 143-147
- [23] Akbulut, H., *et al.*, The Superior Surface Discharge Capacity of Core-Shell Tin oxide/Multi Walled Carbon Nanotube Nanocomposite Anodes for Li-Ion Batteries, *Acta Phys. Pol. A*, 125 (2014), 2, pp. 335-337
- [24] Zhang, J. Wang, X., Microwave Absorbing Property and Preparation of CoNi@SiO₂@PPy Composite in X-Band, *J. Mater. Sci. Mater. Electron.*, 29 (2018), 2, pp. 1592-1599
- [25] Liang, Y., *et al.*, Synthesis and Characterization of Core-Shell Structured SiO₂@YVO₄:Yb³⁺,Er³⁺ Microspheres, *Appl. Surf. Sci.*, 258 (2012), 8, pp. 3689-3694
- [26] Alaf, M., Akbulut, H., Electrochemical Energy Storage Behavior of Sn/SnO₂ Double Phase Nanocomposite Anodes Produced on the Multiwalled Carbon Nanotube Buckypapers for Lithium-Ion Batteries, *J. Power Sources*, 247 (2014), Feb., pp. 692-702
- [27] Zhou, S., *et al.*, SnO₂ Anchored in S and N Co-Doped Carbon as the Anode for Long-Life Lithium-Ion Batteries, *Nanomaterials*, 12 (2022), 4, 700
- [28] Li, H., *et al.*, Porous SNO₂ hollow Microspheres as Anodes for High-Performance Lithium Ion Battery, *Mater. Lett.*, 217 (2018), Apr., pp. 276-280
- [29] Liu, M., *et al.*, Octahedral Tin Dioxide Nanocrystals Anchored on Vertically Aligned Carbon Aerogels as High Capacity Anode Materials for Lithium-Ion Batteries, *Nat. Publ. Gr.*, 6 (2016), Aug., 31496
- [30] Zhang, D., *et al.*, One-Step Synthesis of SnO₂/carbon Nanotube Nanonests Composites by Direct Current Arc-Discharge Plasma and Its Application in Lithium-Ion Batteries, *Nanomaterials*, 11 (2021), 11, 3138
- [31] Jiang, S., *et al.*, Free-Standing SnO₂@rGO Anode via the Anti-solvent-assisted Precipitation for Superior Lithium Storage Performance, *Front. Chem.*, 7 (2019), Dec., pp. 1-10
- [32] Ma, D., *et al.*, Novel Hollow SnO₂ Nanosphere @ TiO₂ 2-Yolk-Shell Hierarchical Nano-Spheres as Anode Material for High-Performance Lithium-Ion Batteries, *Mater. Lett.*, 157 (2015), Oct., pp. 228-230
- [33] Zhang, B., *et al.*, SnO₂-Graphene-Carbon Nanotube Mixture for Anode Material with Improved Rate Capacities, *Carbon N. Y.*, 49 (2011), 13, pp. 4524-4534
- [34] Kebede, M. A., Tin Oxide-Based Anodes for Both Lithium-Ion and Sodium-Ion Batteries, *Curr. Opin. Electrochem.*, 21 (2020), 1, pp. 182-187
- [35] Li, B., *et al.*, Yolk-Shelled SnO₂@NxC Spheres with Controllable Void Space as High-Capacity and Cycle-Stable Anode Materials for Lithium-Ion Batteries, *Mater. Des.*, 219 (2022), July, 110745

- [36] Zhou, D., *et al.*, Three-Dimensional Porous Graphene-Encapsulated CNT@SnO₂ composite for High-Performance Lithium and Sodium Storage, *Electrochim. Acta*, 230 (2017), Mar., pp. 212-221
- [37] Dhanabalan, A., *et al.*, Porous SnO₂/CNT Composite Anodes: Influence of Composition and Deposition Temperature on the Electrochemical Performance, *J. Mater. Res.*, 25 (2010), 8, pp. 1554-1560
- [38] Zhu, S., *et al.*, Precise Growth of Al₂O₃/SnO₂/CNT Composites by a Two-Step Atomic Layer Deposition and Their Application as an Improved Anode for Lithium Ion Batteries, *Electrochim. Acta*, 319 (2019), Oct., pp. 490-498