Graphene nanoscroll/nanosheet aerogels with confined SnS 2 nanosheets : simultaneous wrapping and bridging for high-performance lithium-ion battery anodes

Zhang, Youfang; Zhao, Chenyang; Zeng, Zhihui; Ang, Jia Ming; Che, Boyang; Wang, Zhe; Lu, Xuehong

2018

Zhang, Y., Zhao, C., Zeng, Z., Ang, J. M., Che, B., Wang, Z., et al. (2018). Graphene nanoscroll/nanosheet aerogels with confined SnS 2 nanosheets : simultaneous wrapping and bridging for high-performance lithium-ion battery anodes. *Electrochimica Acta*, 278, 156-164.

<https://hdl.handle.net/10356/89374>

<https://doi.org/10.1016/j.electacta.2018.05.031>

© 2018 Elsevier Ltd. This is the author created version of a work that has been peer reviewed and accepted for publication by *Electrochimica Acta*, Elsevier Ltd. It incorporates referee' s comments but changes resulting from the publishing process, such as copyediting, structural formatting, may not be reflected in this document. The published version is available at: [<http://dx.doi.org/10.1016/j.electacta.2018.05.031>].

Graphene nanoscroll/nanosheet aerogels with confined SnS₂ nanosheets: simultaneous wrapping and bridging for high-performance lithium-ion battery anodes

Youfang Zhang ^a, Chenyang Zhao ^b, Zhihui Zeng ^a, Jia Ming Ang ^a, Boyang Che ^a, Zhe Wang ^a, Xuehong Lu ^{a,*}

^a *School of Materials Science and Engineering, Nanyang Technological University, 50 Nanyang Avenue, 639798, Singapore*

^b *School of Chemistry and Environmental Engineering, Shenzhen University, Shenzhen 518060, PR China*

Corresponding Authors

* (X. H. Lu) E-mail: asxhlu@ntu.edu.sg

ABSTRACT

In this paper, we report graphene nanoscrolls bridged by crumpled graphene nanosheets as an effective conductive framework for confining SnS₂ nanosheets for lithium-ion battery (LIB) applications. The nanoscroll/nanosheet hybrid aerogels (GNAs) with confined SnS₂ nanosheets are facilely prepared via fast quenching, freeze-drying and thermal annealing. During quenching, wrapping SnS₂ nanosheets in the nanoscrolls and bridging the one-dimensional nanoscrolls by the two-dimensional nanosheets occur simultaneously, and the ratio of nanoscrolls/nanosheets can be controlled by simply adjusting quenching conditions. The optimized SnS₂/GNA is highly porous with a large specific surface area of 127.1 m² g⁻¹ and multi-scale pore structure, which can effectively prevent SnS₂ aggregation to provide abundant lithiation/delithiation sites, and buffer volumetric change and pulverization of SnS₂ nanosheets. Moreover, the three-dimensional conductive network formed in the hybrid aerogels can remarkably improve its electrical conductivity while providing sufficient channels for the transportation of lithium ions and charges. As a result, the optimized SnS₂/GNA nanocomposite exhibits enhanced electrochemical performance with a high initial reversible capacity (1514.8 mAh g⁻¹ at 0.1 A g⁻¹), excellent rate capacity (665.4 mAh g⁻¹ at 5 A g⁻¹) and good cyclic stability (1050 mA h g⁻¹ at the 50th cycle). This may provide an efficient generic approach for encapsulation of transition metal dichalcogenide materials in conductive nano/micro confined spaces for fabrication of high-performance LIB anodes.

Keywords: *graphene nanoscrolls; transition metal dichalcogenide, aerogel; lithium ion batteries; porous structure*

1. Introduction

Rechargeable lithium-ion batteries (LIBs) with high specific capacity, large power density, and long cyclic life are promising power sources for electric vehicles [1-3]. As an alternative to commercial graphite carbon [4], which exhibits relatively low theoretical capacity (372 mAh g^{-1}), transition metal dichalcogenide (TMD) layered materials [5], such as MoS_2 [6-10], MoSe_2 [11,12], WS_2 [13,14], WSe_2 [15], VS_2 [16,17], FeS_2 [18], SnS_2 [19-23] are widely considered as potential candidates for LIB anode materials because of their unique sandwiched structures and high theoretical capacity. Many types of TMD nanosheets exhibit, however, relatively low electrical conductivity, and poor structural stability during a long period of fast lithiation/delithiation, hampering their practical application as anode materials. Moreover, the nanosheets fabricated in the form of agglomerates usually suffer from limited specific surface area, which affect the accessibility of lithium ions, also resulting in poor electrochemical performance of the anodes.

To address the aforementioned issues, many approaches have been investigated, including optimization of micro/nano-structures of two-dimensional (2D) TMD nanosheets, fabrication of three-dimensional (3D) flower-like microspheres, and confinement of TMD nanosheets in conductive carbonaceous and polymer matrices with large specific surface areas [24-28]. Of the various approaches, the combination of TMD nanosheets with conductive substrates has attracted much attention because of the potential of this approach to improve electrical conductivity, provide large specific surface area and good accessibility to electrolyte and lithium ions, and stabilize the nanocomposite structures to accommodate the volumetric expansion/shrinkage. Research results have shown that graphene is an ideal

1 conductive substrate to disperse and confine active materials because of its excellent
2
3 conductivity, large specific surface area, robust mechanical strength and remarkable stability.
4
5 Nevertheless, owing to their open structure, 2D graphene nanosheets could not confine active
6
7 anode materials very effectively [29]. Hence, another form of graphene, graphene nanoscrolls,
8
9 has recently attracted significant attention. Graphene nanoscrolls are composed of several
10
11 rolled-up graphene nanosheets. They exhibit open-ended tubular hollow structure and hence
12
13 are considered as a much better conductive substrate to confine active materials, while
14
15 tubular cavities can also provide the channels for ion transport. Piao et al. wrapped sulfur
16
17 particles in one-dimensional (1D) reduced graphene oxide nanoscroll (GNSC) by freezing the
18
19 plastic tubes encapsulated with high-temperature precursor suspensions followed by
20
21 freeze-drying for several days [30]. The prepared sulfur/GNSC nanocomposites showed the
22
23 effective confinement effect of GNSC for active materials in lithium-sulfur batteries. In a
24
25 similar way, Xu et al. prepared graphene nanoscroll-wrapped Fe_3O_4 nanoparticles
26
27 ($\text{Fe}_3\text{O}_4@\text{GNSC}$) for LIBs [31]. Despite offering significant confinement effect, graphene
28
29 nanoscrolls are 1D nanomaterials and thus they have a common drawback of 1D
30
31 nanomaterials, i.e., they are more difficult to form effective conductive networks for electron
32
33 transport than 2D nanomaterials.
34
35
36
37
38
39
40
41
42
43
44
45
46

47 To enhance both the confinement effect and electron transport, in this work, for the first
48
49 time we fabricated 3D nanoaerogels composed of graphene nanoscrolls bridged by curved
50
51 graphene nanosheets, and used these nanoscroll/nanosheet hybrid nanoaerogels to confine
52
53 SnS_2 nanosheets for high-performance LIB anodes. As a typical type of TMD nanomaterials,

54
55
56 SnS_2 is is low-cost, non-toxic, easy to be prepared, and exhibits relatively good chemical

stability and high theoretical capacity. Typical SnS_2 nanosheets exhibit layered CdI_2 -type structure composed of tin atoms sandwiched between double layers of close-packed sulfur atoms, which is suitable for fast intercalation/de-intercalation of lithium ions. So far although many SnS_2 -based nanocomposite systems, such as SnS_2 /graphene [20,32,33], SnS_2 /CNT [34], SnS_2 /graphene/CNT [35], SnS_2 /vanadium nitride [36], SnS_2 /conductive polymers [7,37], SnS_2 / SnO_x [21,22,38] have been developed, approaches that can simultaneously promote the confinement effect and conductive network formation for enhancing both structural stability and electron transport has not been demonstrated. In this work, SnS_2 nanosheets were used as a model TMD material to investigate the possibility of simultaneously confining TMD active materials in nanoscrolls and promoting conductive network formation via bridging the nanoscrolls by graphene nanosheets. The motivation was to provide an efficient generic approach for simultaneous enhancing structural stability and electron transport of various TMD nanomaterials for fabrication of advanced electrode materials for lithium-ion batteries.

Our highly porous SnS_2 -encapsulated graphene nanoscroll/nanosheet nanoaerogel (SnS_2 /GNA) contains controllable amounts of hollow tubular graphene nanoscrolls and curved graphene nanosheets. The inter-connected tubular graphene nanoscrolls and curved graphene nanosheets form 3D networks, which not only offer abundant conductive channels for the transport of lithium ions and charges, but also provide spacious inter-space to buffer SnS_2 nanosheet volumetric expansion/shrinkage and pulverization during the repeated lithiation/delithiation in cycling tests. As a result, the optimized SnS_2 /GNA nanocomposite exhibits a high initial reversible capacity ($1514.8 \text{ mAh g}^{-1}$ at 0.1 A g^{-1}), excellent rate capacity (665.4 mAh g^{-1} at a high current density of 5 A g^{-1}) and good cyclic stability. The

superior electrochemical performance with high reversible capacity, high coulombic efficiency, good cycling and rate capability makes SnS₂/GNA as a promising anode material for LIBs.

2. Experimental section

2.1. Materials

Natural graphite powder with the size of 325 mesh was obtained from Alfa-Aesar. 98% H₂SO₄, 30% H₂O₂, KMnO₄, 37% HCl, KOH, tin (IV) chloride pentahydrate, and thioacetamide were purchased from Sinopharm Chemical Reagent Co., Ltd. Deionized (DI) water was used as the solvent throughout the experiments.

2.2. Preparation of SnS₂ nanosheets, SnS₂/GNAs, and GNA

Neat SnS₂ nanosheets were synthesized by adopting a reported hydrothermal method [35]. Graphene oxide (GO) powder was prepared from natural graphite powder using Hummer's chemical oxidation method [39]. The well exfoliated GO suspension with 0.5 mg mL⁻¹ was prepared by continuous ultrasonication of GO powder in DI water for 3 h. The SnS₂/GNAs with different amount of SnS₂ nanosheets were fabricated by the processes of cold quenching, freeze-drying, and thermal annealing as schematically shown in Scheme 1. Typically, pure SnS₂ nanosheets were dispersed in the as-prepared GO suspension by continuous ultrasonication, and the weight ratios of pure SnS₂ nanosheets and GO nanosheets are 1:2, 1:1 and 2:1. Then, the mixed dispersion was dropped into liquid nitrogen to fabricate 3D GO nanoscroll/nanosheet wrapped and encapsulated SnS₂ networks. After that, the obtained frozen globules were quickly dried in a lyophilizer to obtain SnS₂/GO

nanocroll/nanosheet nanoaerogels ($\text{SnS}_2/\text{GONAs}$), and donated as $\text{SnS}_2/\text{GONA-0.5}$, $\text{SnS}_2/\text{GONA-1}$, and $\text{SnS}_2/\text{GONA-2}$, respectively. In order to reduce GO to graphene and perfect crystalline structure of SnS_2 , the as-prepared $\text{SnS}_2/\text{GONAs}$ was calcined at 350 °C for 2 h under N_2 atmosphere. The SnS_2/GNAs with GO to SnS_2 weight ratio of 1/2, 1/1 and 2/1 are labelled as $\text{SnS}_2/\text{GNA-0.5}$, $\text{SnS}_2/\text{GNA-1}$, and $\text{SnS}_2/\text{GNA-2}$, respectively. Moreover, pure GNA was prepared by the aforementioned process with any SnS_2 nanosheets.

2.3. Characterization

The structures and morphologies of the as-prepared samples were investigated by a field emission scanning electron microscopy (FESEM, JEOL JSM 7600) at an acceleration voltage of 5 kV and a transmission electron microscope (TEM, JEOL 2100) at 200 kV. X-ray diffraction (XRD) patterns were recorded on a Bruker GADDS X-ray diffractometer with $\text{CuK}\alpha$ radiation ($\lambda = 0.1542 \text{ nm}$) from $2\theta=5^\circ$ to 80° at the voltage of 40 kV and current of 40 mA. X-ray photoelectron spectroscopy (XPS) measurements were collected on a device of Kratos Analytical AXIS with a monochromatized Al Ka X-ray source (1486.6 eV photons). TEM and XRD studies were also carried out to examine the structure and morphology of $\text{SnS}_2/\text{GNA-1}$ after 50 cycles of charge/discharge. Before the examination, the electrodes were washed with acetone for several times to eliminate the electrolyte and residues. All XPS spectra were corrected using C1s line at 284.5 eV. Thermogravimetric analysis (TGA, TA Q500) was conducted under air flow from 100 to 800 °C at a heating rate of 20 °C min^{-1} . The specific surface area and pore size distribution were characterized by a surface area and porosity test instrument (Micromeritics, Tristar II 3020) by N_2 physisorption at 77 K.

2.4. Electrochemical measurements

The as-prepared electrode materials (pure SnS₂ nanosheets, SnS₂/GNAs, and pure GNA) were assembled into standard CR2032 coin cells in an argon filled glovebox. In these coin cell electrodes, Celgard 2400 film was used as separator, lithium foils were applied as counter electrodes, and LiPF₆ (1M) in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1/1 in v/v) was used as the electrolytes. The working electrodes were prepared from a slurry composited of 80 wt% the obtained samples prepared in this work, 10 wt% carbon black as conductive additives and polyvinylidene fluoride (PVDF) as binders. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements were performed via a PGSTAT302N Autolab electrochemical workstation. The potential and scan rate of CV testes are 0.005 to 3.0 V, 0.1 mV s⁻¹. EIS was measured in the frequency range from 0.01 Hz to 100 kHz at an open circuit potential with amplitude of 5 mV. Galvanostatic charge/discharge curves were performed through a NEWAREBTS-5 V 10 mA battery tester device.

3. Results and discussion

3.1. Structures and morphologies

The preparation process for SnS₂/GNAs is schematically illustrated in Scheme 1. Thin SnS₂ nanosheets were first synthesized according to the reported method [35]. The obtained SnS₂ nanosheets were dispersed in a low-concentration GO suspension. The nanosheets were quickly encapsulated and wrapped by GO sheets and formed 3D highly porous SnS₂/GONAs when quenching using liquid nitrogen. In this process, the GO nanosheets wrapped with SnS₂

1 nanosheets curved and scrolled owing to the tremendous temperature gradient. After thermal
2
3 annealing at 350 °C, GONAs were reduced into GNAs and the crystalline structure of SnS₂
4
5 was optimized simultaneously.
6
7

8
9 SEM images (Fig. 1a-d) of neat GONAs reveal that a number of tubular structures
10
11 connected with curly and crumpled edges of GO nanosheets are generated by the partial
12
13 rolling-up GO nanosheets during quenching. The corresponding TEM images in Fig. 1e,f also
14
15 verify that the GONAs obtained are indeed nanoscroll/nanosheet hybrid structures. GO
16
17 nanoscrolls are well connected with highly corrugated GO nanosheets, forming highly porous
18
19 3D networks, which can act as effective conductive frameworks. The scheme at the bottom of
20
21 Fig. 1 illustrates how a GO nanosheet is transformed into a GO nanoscroll in liquid nitrogen.
22
23 The thin edges and corners of the GO sheet curl first to accommodate the strong cooling
24
25 effect caused by the huge temperature change. The resultant surface strain along with the
26
27 rapid bubbling caused by the heat released from the GO nanosheets then induce
28
29 self-assembly of 2D nanosheets into 1D nanoscrolls. As the time goes on, small single-layer
30
31 and few-layer GO nanosheets roll up to form single-walled and multi-walled GO nanoscrolls,
32
33 respectively [40], whereas large and thick GO sheets cannot scroll and hence retain their
34
35 sheet-like morphology. Therefore, a hybrid of GO nanoscrolls and nanosheets could be
36
37 fabricated by rapid quenching in liquid nitrogen.
38
39
40
41
42
43
44
45
46
47
48
49

50 Fig. 2 shows the morphologies of SnS₂/GNAs with different amounts of encapsulated
51
52 SnS₂ nanosheets. The top-view SEM images of SnS₂/GNAs show hierarchical porous
53
54 structures with curved nanosheets and tubular nanoscrolls. Moreover, SnS₂ nanosheets are
55
56 fully anchored on the surface and inside of graphene nanosheets and nanoscrolls. It can be
57
58
59
60

clearly seen that the amount of SnS₂ nanosheets greatly affects the morphology of the resultant hybrid aerogels. With the increased amount of SnS₂ nanosheets, the ratio of tubular nanoscrolls to nanosheets increases, indicating that the addition of SnS₂ nanosheets promotes the formation of tubular nanoscroll structure. The possible reason can be ascribed to the changes of GO surface. With the SnS₂ nanosheets attached on the surface of ultra-thin GO nanosheets, especially single-layer GO nanosheets, GO nanosheets may distort more quickly. Thus, as the amount of SnS₂ nanosheets increases, more and more nanoscrolls are formed. Moreover, the nanoscrolls and curved nanosheets are connected and twined with the adjacent ones, forming 3D conjoint branches to minimize the total surface energy. However, SnS₂ nanosheets in SnS₂/GNA-2 seem to aggregate seriously due to excess SnS₂ nanosheets loaded. Thus, the optimal ratio of SnS₂ nanosheets/GO nanosheets is 1/1 in this work owing to the limited active sites on GO nanosheets for attachment of SnS₂. The TEM image of SnS₂/GNA-1 also reveals that SnS₂ nanosheets are evenly wrapped/attached both inside and outside of GNA (Fig. S1a), which is in accordance with SEM images. The HRTEM image of a typical SnS₂ nanosheet encapsulated in GNA shows a typical lamellar structure with seven sandwiched S-Sn-S layers (Fig. S1b). The inter-planar spacing is 0.41 nm, which is indexed to the (001) plane of SnS₂. As shown in Fig. S2, SnS₂ nanosheets without GNA aggregate severely, implying the importance of the graphene substrates for effectively preventing the aggregation of SnS₂ nanosheets. The superiority of SnS₂/GNA-1 in pore structure and specific surface area over neat SnS₂ is also evidenced by the surface area measurements via nitrogen physisorption (Fig. 3). It is obvious that both isotherm curves of neat SnS₂ and SnS₂/GNA-1 belong to IV type with a clear hysteresis loop (Fig. 3a). The Langmuir specific

surface areas of SnS₂/GNA-1 is 127.1 m² g⁻¹, which is much larger than that of neat SnS₂ (18.5 m² g⁻¹). Compared with the narrow pore size of neat SnS₂, which is centered at 145 nm, SnS₂/GNA-1 exhibits a much wider pore size distribution, ranging from 20 nm to 1000 nm and centered at 38 nm, 138 nm, and 204 nm, respectively (Fig. 3b). The multiscale pore structure benefits the accessibility of the electrode materials by the electrolyte and fast transport of lithium ions and charges, enhancing the electrochemical performance. Moreover, the morphology of SnS₂/GNAs can be easily controlled by modulating the quenching conditions. For example, for SnS₂/GNA-1, by increasing the temperature of the mixed suspension, the amount of nanoscrolls can be increased greatly (Fig. S3).

The crystal structures of GO nanosheets, GNA, neat SnS₂ nanosheets and SnS₂/GNA-1 were investigated via X-ray diffraction (Fig. 4a). GO nanosheets show a diffraction peak at $2\theta = 10.7^\circ$ while GNA exhibits two diffraction peaks at $2\theta = 26^\circ$ and $2\theta = 44^\circ$, confirming that GO nanosheets have been completely reduced into graphene by thermal annealing. In the XRD patterns of both neat SnS₂ nanosheets and SnS₂/GNA-1, relatively strong diffraction peaks can be observed at $2\theta = 15.3^\circ$, 28.8° , 32.5° , 50.4° and 52.8° , which can be indexed to (001), (100), (101), (110) and (111) planes of SnS₂, respectively. Besides, a weak diffraction peak centered at $2\theta = 26^\circ$ for SnS₂/GNA-1 confirms the presence of GNA; the peak is very weak due to the intensive diffraction of the highly crystalline SnS₂, which conceals the diffraction of GNA. Thus, the XRD patterns suggest that SnS₂ nanosheets with good phase purity are successfully incorporated into GNA. Additionally, the loading amounts of SnS₂ nanosheets in SnS₂/GNAs are also studied using TGA (Fig. 4b). As calculated from TGA curves, the weight ratio of SnS₂ nanosheets in SnS₂/GNA-0.5, SnS₂/GNA-1 and SnS₂/GNA-2

are 55.2%, 68.8%, and 79.1%, respectively. The elements of C, Sn, O, and S co-exist in SnS₂/GNA-1, which is confirmed by XPS survey spectrum (Fig. S4). In the high-resolution spectrum of Sn 3d, the peaks centered at 486.5 and 494.8 eV are related to Sn 3d_{5/2} and Sn 3d_{3/2}. As seen in S 2p spectrum, the peaks centered at 161.7 and 162.7 eV are related to S 2p_{1/2} and S 2p_{3/2}. Therefore, the spectrum of Sn 3d and S 2p confirms the presence of SnS₂ in the nanocomposite of SnS₂/GNA-1.

3.2. Electrochemical performances

In this work, highly porous GNA with hierarchical nanoscroll/nanosheet structures is used as a 3D conductive substrate for encapsulation SnS₂ nanosheets without aggregation. The CV curves, galvanostatic discharge/charge curves, rate and cycle stability, and EIS were obtained using a two-electrode cell with lithium foil as the counter electrode. Initially, the lithiation/delithiation behaviors of SnS₂/GNAs were examined via CV curves (Fig. 5a) and galvanostatic discharge/charge curves (Fig. 5b) in the first, second, and third cycles, taking SnS₂/GNA-1 electrode as an example. During the first CV cycle, the reduction peaks at 1.57, 1.31, 1.10, and 1.03 V (vs. Li⁺/Li) represent the lithium intercalation of SnS₂ layers, the decomposition of SnS₂ into metallic tin, and the formation of Li₂S (equation 1 and equation 2), respectively. Among these reduction peaks, the peaks at 1.10, 1.03 V are not observed in the subsequent cycles, showing that they correspond to the lithium intercalation of SnS₂ layers without phase decomposition (equation 1), which results in irreversible loss of capacity in the first cycle. Moreover, the reduction peak at 0.70 V may be attributed to a reaction of lithium ions with GNA, which can be observed in the first cycle of GNA (Fig. S5). The oxidation peaks in the region of 0.50 V to 2.5 V mainly represent the reversible and

irreversible delithiation reaction of Li_xSn alloys (equation 3). Among these oxidation peaks, the peak at 1.23 probably corresponds to the delithiation reaction of lithium-based composite derived from the reaction of lithium ions with GNA (equation 4). Similarly, in the initial lithiation curve of $\text{SnS}_2/\text{GNA-1}$ electrode (Fig. 5a) during the discharge process, the potential plateaus (1.57 V and 1.31 V) belong to lithiation of SnS_2 into Sn nanoparticles and Li_xSn , while the potential plateaus from 0.50 V to 2.5 V during the charge process are mainly due to the delithiation of Li_xSn alloys. These observations are consistent with their corresponding CV curves.

To better understand the differences in the electrochemical behaviors of neat SnS_2 and SnS_2/GNAs , rate performances are further investigated by analyzing galvanostatic discharge/charge curves at different current densities. As seen in Fig. 6, the discharge capacities of these materials all reduce with the increase of the current density, indicating that the diffusion-controlled kinetics process is the main process for the electrochemical reactions. The reversible capacity of neat SnS_2 electrode exhibits a discharge capacity of only 16.6 mAh g^{-1} at the rate of 2 A g^{-1} , 2.3% of the original capacity. Moreover, the electrode does not work when the current density is reduced back to 0.1 A g^{-1} . By contrast, benefiting from the confinement effect provided by the porous GNA matrix, the rate performances of all the SnS_2/GNA electrodes are better than that of neat SnS_2 electrode. Specifically, the reversible

capacity of the optimized SnS₂/GNA-1 electrode is able to deliver a discharge capacity of 495-506 mAh g⁻¹ even at a high rate of 10 A g⁻¹, which is restored to 1353.2 mAh g⁻¹ as the current density changes back to 0.1 A g⁻¹. Besides, the first-cycle coulombic efficiency of the optimized anode is about 65.5%, whereas in the following cycles, the coulombic efficiency quickly approaches 93-96%. The results indicate that SnS₂/GNA electrodes could tolerate varied current densities and thus is a promising anode candidate for LIBs.

Long-term cyclic stability is a very important property for LIB anodes. The cyclic behaviors of neat SnS₂ nanosheets, GNA and SnS₂/GNAs were characterized by testing galvanostatic discharge/charge curves at a current density of 0.1 A h g⁻¹ for 50 cycles (Fig. 7a). GNA exhibits excellent specific capacity of 651.5 mAh g⁻¹ at the first cycle as well as outstanding cyclic behavior compared with the previously reported graphene-based materials. This can be ascribed to the unique morphology of the 3D interconnected graphene nanoscrolls and wrinkled thin graphene nanosheets, which can offer continuous and low-resistance transport paths for lithium ions. Neat SnS₂ nanosheets, on the other hand, show poor cyclic behavior, i.e., the discharge capacity reduces greatly from 736.4 mA h g⁻¹ at the first cycle to 92.0 mA h g⁻¹ at the 50th cycle. Fast capacity decay of neat SnS₂ nanosheets is mainly due to the severe aggregation of the nanosheets, their poor electrical conductivity, and pulverization during the long-term cyclic testing. Compared with both GNA and neat SnS₂ nanosheets, the reversible capacity of SnS₂/GNAs are greatly enhanced by utilizing the wrapping and confinement effect of GNA. Specially, the optimized nanocomposite of SnS₂/GNA-1 reaches 1050 mA h g⁻¹ at the 50th cycle, showing a high capacity retention of 69.3%. The overall electrochemical performance of SnS₂/GNA-1 reported in this paper is

1 better than those of other SnS₂/graphene-based composites as electrode materials reported in
2
3 literature (Table S1). The enhanced overall performance of SnS₂/GNA-1 can be ascribed to
4
5 their unique morphological features. On one hand, the porous GNA with large specific
6
7 surface area and multiscale pore structure can provide abundant lithiation/delithiation sites
8
9 while buffering the volume change during the intercalation and de-intercalation of lithium
10
11 ions to prevent disintegration of the two components. On the other hand, the nanoscrolls are
12
13 effectively connected by the severely corrugated nanosheets, forming interconnected and
14
15 interpenetrated 3D conductive networks, which can remarkably improve the electrical
16
17 conductivity of the GNA while providing sufficient channels for fast lithium ion diffusion.
18
19
20
21
22
23
24

25 To investigate the mechanism for the good long-term cyclic stability of SnS₂/GNA-1, the
26
27 electrode was examined by TEM (Fig. 7b-c) and XRD (Fig. 7d) after 50 cycles of
28
29 charge/discharge. In Fig. 7b-c, both 1D graphene nanoscrolls and curved 2D graphene
30
31 nanosheets can be clearly observed. They are interconnected with one another, forming a 3D
32
33 network. After the cycling, nanoparticles, instead of SnS₂ nanosheets, are confined in the
34
35 graphene nanoscroll/nanosheet aerogel (Fig. 7c). This is due to the lithium intercalation of
36
37 SnS₂ layers, the decomposition of SnS₂ into metallic tin, the formation of Li₂S, Li_xSnS₂,
38
39 Li_xSn, and Li_xC, as shown in the reaction equations 1 to 4. Because of these reactions,
40
41 especially the reactions in equation 1 and 2, SnS₂ nanosheets are converted to
42
43 lithium-containing nanoparticles. XRD was used to verify the presence of lithium composites.
44
45 In the XRD pattern of SnS₂/GNA-1 after 50 cycles, the relatively strong diffraction peaks at
46
47 $2\theta = 43.5^\circ$, 50.6° and 74.2° are due to the Cu foil, which was used as the conductive collector
48
49 and the XRD sample was tested on its surface without peeled off. The three weak diffraction
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

peaks between 20° to 40° can also be observed. By further zooming in this part of the XRD pattern, diffraction peaks centered at $2\theta = 22.2^\circ$, 31.1° and 37.0° , respectively, can be identified, which are indexed to the planes of Li_xSn , LiS_2 , and Li , respectively. The XRD result agrees well with the reaction equations and TEM images. Thus, owing to the stable 3D network structure of graphene nanoscroll/nanosheet and the excellent confinement effect, no significant amount of inactive by-products are not produced and hence the optimized $\text{SnS}_2/\text{GNA}-1$ exhibits good cyclic stability.

In order to better understand the enhanced electrochemical performance of SnS_2/GNAs , EIS measurements were conducted for neat SnS_2 nanosheets, GNA, and SnS_2/GNAs (Fig. 8). The Nyquist plots of neat SnS_2 electrode consists of two semicircles in high and medium frequency regions, respectively, and a straight line inclined at a constant angle in low frequency region, while those of GNA and SnS_2/GNA electrodes consist of one depressed semicircle in high frequency region and one inclined line in low frequency region. Specially, the semicircles represent the resistance (R_f) and constant phase element (CPE_f) of the SEI film, the constant phase element (CPE_{ct}) of the electrode/electrolyte interface, the internal resistance (R_e) of the battery, and the charge transfer resistance (R_{ct}). The inclined line in low frequency region is associated with the Warburg impedance (Z_w) related to the solid-state diffusion resistance of lithium ions in the electrode. Obviously, with the increase of GNA content, the radius of the semicircle and the intersect of the Nyquist plots with the real axis in the range of high and medium frequencies reduce significantly, which signify a remarkable reduction of R_{ct} , suggesting the enhanced conductivity. Moreover, with the increase of GNA content, the slope of Warburg line increases greatly, indicating that the lithium ion diffusion

1 becomes much faster in the GNA-based nanocomposites. Thus, graphene encapsulating and
2
3 wrapping leads to remarkably enhanced conductivity of the nanocomposites and much faster
4
5 transport of lithium ions during the process of lithiation/delithiation, resulting a significant
6
7 improvement of lithium storage performance.
8
9

10 11 12 13 14 **4. Conclusions** 15

16
17 In this work, a novel anode material for LIBs was readily synthesized via encapsulation
18
19 and confinement of SnS₂ nanosheets in highly porous and conductive GNAs. In the resultant
20
21 nanocomposites, SnS₂ nanosheets are uniformly dispersed and wrapped in interconnected
22
23 GNA substrates. This effectively hampers aggregation, volumetric excursion and
24
25 pulverization of SnS₂ nanosheets. Moreover, the highly porous GNA composed of hollow
26
27 tubular graphene nanoscrolls and crumpled graphene nanosheets can offer abundant
28
29 conductive channels for the transport of lithium ions and charges. Thus, the optimized
30
31 nanocomposite, SnS₂/GNA-1, exhibits impressive electrochemical performance with a
32
33 capacity of 1514.8 mAh g⁻¹ at 0.1 A g⁻¹ and excellent rate capacity of 665.4 mAh g⁻¹ at a high
34
35 current density of 5 A g⁻¹. Furthermore, the preparation method used is simple and scalable.
36
37 Hence, the large-scale preparation of SnS₂/GNA is a promising approach to high performance
38
39 anode materials for LIBs.
40
41
42
43
44
45
46
47
48
49
50
51
52

53 **Acknowledgements** 54 55 56 57 58 59 60 61 62 63 64 65

The authors thank Agency for Science, Technology and Research and Nanyang Technological University, Singapore for providing PhD scholarships and funding in the course of this work.

Notes

The authors declare no competing financial interest.

Appendix A. Supplementary data

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.electacta.XXXX.XX.XXX>.

References

- [1] J.W. Choi, D. Aurbach, Promise and reality of post-lithium-ion batteries with high energy densities, *Nat. Rev. Mater.* 1 (2016) 16013-16029.
- [2] Y. M. Sun, N. Liu, Y. Cui, Promises and challenges of nanomaterials for lithium-based rechargeable batteries, *Nat. Energy* 1 (2016) 16071-16083.
- [3] J. M. Tarascon, M. Armand, Issues and challenges facing rechargeable lithium batteries, *Nature* 414 (2001) 359-367.
- [4] H. Buqa, D. Goers, M. Holzapfel, M. E. Spahr, P. Novak, High rate capability of graphite negative electrodes for lithium-ion batteries, *J. Electrochem. Soc.* 152 (2005) 474-481.
- [5] B. Liu, J. G. Zhang, G. Z. Shen, Pursuing two-dimensional nanomaterials for flexible lithium-ion batteries, *Nano Today* 11 (2016) 82-97.

- [6] J. W. Zhou, J. Qin, X. Zhang, C. S. Shi, E. Z. Liu, J. J. Li, et al., 2D space-confined synthesis of few-layer MoS₂ anchored on carbon nanosheet for lithium-ion battery anode, ACS Nano 9 (2015) 3837-3848.
- [7] J. Liu, M. Z. Gu, L. Z. Quyang, H. Wang, L. C. Yang, M. Zhu, Sandwich-like SnS/polypyrrole ultrathin nanosheets as high-performance anode materials for li-ion batteries, ACS Appl. Mater. Interfaces 8 (2016) 8502-8510.
- [8] Y. E. Miao, Y. P. Huang, L. S. Zhang, W. Fan, F. L. Lai, T. X. Liu, Electrospun porous carbon nanofiber@MoS₂ core/sheath fiber membranes as highly flexible and binder-free anodes for lithium-ion batteries, Nanoscale 7 (2015) 11093-11101.
- [9] C. Y. Zhao, X. Wang, J. H. Kong, J. M. Ang, P. S. Lee, Z. L. Liu, et al., Thin MoS₂ nanoflakes encapsulated in carbon nanofibers as high-performance anodes for lithium-ion batteries, ACS Appl. Mater. Interfaces 6 (2014) 6392-6398.
- [10] J. H. Kong, C. Y. Zhao, Y. F. Wei, X. H. Lu, MoS₂ nanosheets hosted in polydopamine-derived mesoporous carbon nanofibers as lithium-ion battery anodes: enhanced MoS₂ capacity utilization and underlying mechanism, ACS Appl. Mater. Interfaces 7 (2015) 24279-24287.
- [11] H. Wang, X. Y. Wang, L. Wang, J. Wang, D. L. Jiang, G. P. Li, et al., Phase transition mechanism and electrochemical properties of nanocrystalline MoSe₂ as anode materials for the high performance of lithium-ion battery, J. Phys. Chem. C 119 (2015) 10197-10205.
- [12] Y. Liu, M. Q. Zhu, D. Chen, Sheet-like MoSe₂/C composites with enhanced li-ion storage properties, J. Mater. Chem. A 3 (2015) 11857-11862.

- [13] R. J. Chen, T. Zhao, W. P. Wu, F. Wu, L. Li, J. Qian, et al. Free-standing hierarchically sandwich-type tungsten disulfide nanotubes/graphene anode for lithium-ion batteries, *Nano Lett.* 14 (2014) 5899-5904.
- [14] X. H. Zeng, Z. P. Ding, C. Ma, L. D. Wu, J. T. Liu, L. B. Chen, et al, Hierarchical nanocomposite of hollow N-doped carbon spheres decorated with ultrathin WS₂ nanosheets for high-performance lithium-ion battery anode, *ACS Appl. Mater. Interfaces* 8 (2016) 18841-18848.
- [15] F. J. Chen, J. Wang, B. Li, C. H. Yao, H. F. Bao, Y. F. Shi, Nanocasting synthesis of ordered mesoporous crystalline WSe₂ as anode material for li-ion batteries, *Mater. Lett.* 136 (2014) 191-194.
- [16] W. Y Fang, H. B. Zhao, Y. P. Xie, J. H. Fang, J. Q. Xu, Z. W. Chen, Facile hydrothermal synthesis of VS₂/graphene nanocomposites with superior high-rate capability as lithium-ion battery cathodes, *ACS Appl. Mater. Interfaces* 7 (2015) 13044-13052.
- [17] Y. Jing, Z. Zhou, C. R. Cabrera, Z. F. Chen, Metallic VS₂ monolayer: a promising 2D anode material for lithium ion batteries, *J. Phys. Chem. C* 117 (2013) 25409-25413.
- [18] J. R. He, Q. Li, Y. F. Chen, C. Xu, K. Zhou, X. Q. Wang, et al, Self-assembled cauliflower-like FeS₂ anchored into graphene foam as free-standing anode for high-performance lithium-ion batteries, *Carbon* 114 (2017) 111-116.
- [19] W. Shi, B. G. Lu, Nanoscale kirkendall effect synthesis of echinus-like SnO₂@SnS₂ nanospheres as high performance anode material for lithium ion batteries. *Electrochim. Acta* 133 (2014) 247-253.

- [20] D. H. Youn, S. K. Stauffer, P. H. Xiao, H. M. Park, Y. J. Nam, A. Dolocan, et al, Simple synthesis of nanocrystalline tin sulfide/N-doped reduced graphene oxide composites as lithium ion battery anodes. *ACS Nano* 10 (2016) 10778-10788.
- [21] Y. Q. Zhang, Z. L. Ma, D. D. Liu, S. Dou, J. M. Ma, M. Zhang, et al, p-type SnO thin layers on n-type SnS₂ nanosheets with enriched surface defects and embedded charge transfer for lithium ion batteries, *J. Mater. Chem. A* 5 (2017) 512-518.
- [22] L. X. Yin, S. M. Chai, J. F. Huang, X. G. Konh, L. M. Pan, Preparation of hierarchical SnS₂/SnO₂ anode with enhanced electrochemical performances for lithium-ion battery, *Electrochim. Acta* 238 (2017) 168-177.
- [23] D. S. Guan, L. L. Ma, D. Q. Pan, J. Y. Li, X. F. Gao, Y. Y. Xie, et al, Atomic layer deposition of alumina coatings onto SnS₂ for lithium-ion battery applications, *Electrochim. Acta* 24 (2017) 117-124.
- [24] Z. Liu, H. Deng, P. P. Mukherjee, Evaluating pristine and modified SnS₂ as a lithium-ion battery anode: a first-principles study, *ACS Appl. Mater. Interfaces* 7 (2015) 4000-4009.
- [25] Y. P. Du, Z. Y. Yin, X. H. Rui, Z. Y. Zeng, X. J. Wu, J. Q. Liu, et al. A facile, relative green, and inexpensive synthetic approach toward large-scale production of SnS₂ nanoplates for high-performance lithium-ion batteries, *Nanoscale* 5 (2013) 1456-1459.
- [26] X. Jiang, X. L. Yang, Y. H. Zhu, J. H. Shen, K. C. Fan, C. Z. Li, In situ assembly of graphene sheets-supported SnS₂ nanoplates into 3D macroporous aerogels for high-performance lithium ion batteries, *J. Power Sources* 237 (2013) 178-186.

- [27] G. X. Wang, X. P. Shen, J. Yao, J. S. Park, Graphene nanosheets for enhanced lithium storage in lithium ion batteries, *Carbon* 47 (2009) 2049-2053.
- [28] Q. Wu, L. F. Jiao, J. Du, J. Q. Yang, L. J. Guo, Y. C. Liu, et al., One-pot synthesis of three-dimensional SnS₂ hierarchitectures as anode material for lithium-ion batteries, *J. Power Sources* 239 (2013) 89-93.
- [29] L. S. Zhang, W. Fan, T. X. Liu, A flexible free-standing defect-rich MoS₂/graphene/carbon nanotube hybrid paper as a binder-free anode for high-performance lithium ion batteries, *RSC Adv.* 5 (2015) 43130-43140.
- [30] S. Y. Yoo, J. Y. Lee, J. M. Kim, C. Y. Seong, K. D. Seong, Y. Z. Piao, Well-dispersed sulfur wrapped in reduced graphene oxide nanoscroll as cathode material for lithium-sulfur battery, *J. Electroanal. Chem.* 780 (2016) 19-25.
- [31] B. J. Yang, J. P. Zhao, J. T. Chen, M. He, S. Xu, Controllable synthesis of graphene nanoscroll-wrapped Fe₃O₄ nanoparticles and their lithium-ion battery performance, *RSC Adv.* 5 (2015) 57906-57911.
- [32] B. H. Qu, C. Ma, G. Ji, C. H. Xu, J. Xu, Y. S. Meng, et al., Layered SnS₂-reduced graphene oxide composite-a high-capacity, high-rate, and long-cycle life sodium-ion battery anode material, *Adv. Mater.* 26 (2014) 3854-3859.
- [33] Q. Q. Zhang, R. Li, M. M. Zhang, B. L. Zhang, X. L. Gou, SnS₂/reduced graphene oxide nanocomposites with superior lithium storage performance, *Electrochim. Acta* 115 (2014) 425-433.

- [34] H. Y. Sun, M. Ahmad, J. Luo, Y. Y. Shi, W. C. Shen, J. Zhu, SnS₂ nanoflakes decorated multiwalled carbon nanotubes as high performance anode materials for lithium-ion batteries, Mater. Res. Bull. 49 (2014) 319-324.
- [35] L. S. Zhang, Y. P. Huang, Y. F. Zhang, W. Fan, T. X. Liu, Three-dimensional nanoporous graphene-carbon nanotube hybrid frameworks for confinement of SnS₂ nanosheets: flexible and binder-free papers with highly reversible lithium storage, ACS Appl. Mater. Interfaces 7 (2015) 27823-27830.
- [36] M. S. Balogun, W. T. Qiu, J. H. Jian, Y. C. Huang, Y. Luo, H. Yang, et al., Vanadium nitride nanowire supported SnS₂ nanosheets with high reversible capacity as anode material for lithium ion batteries, ACS Appl. Mater. Interfaces 7 (2015) 23205-23215.
- [37] G. Wang, J. Peng, L. L. Zhang, J. Zhang, B. Dai, M. Y. Zhu, et al., Two-dimensional SnS₂@PANI nanoplates with high capacity and excellent stability for lithium-ion batteries, J. Mater. Chem. A 3 (2015) 3659-3666.
- [38] W. W. Xu, Z. Q. Xie, X. D. Cui, K. N. Zhao, L. Zhang, G. Dietrich, Hierarchical graphene-encapsulated hollow SnO₂@SnS₂ nanostructures with enhanced lithium storage capability, ACS Appl. Mater. Interfaces 7 (2015) 22533-22541.
- [39] W. S. Hummers, R. E. Offeman, Preparation of graphitic oxide, J. Am. Chem. Soc. 80 (1958) 1339.
- [40] Z. C. Lai, Y. Chen, C. L. Tan, X. Zhang, H. Zhang, Self-assembly of two-dimension nanosheets into one-dimension nanostructures. Chem. 1 (2017) 59-77.

Figure Caption

Scheme 1. Schematic illustration of the preparation of GNA and SnS₂/GNA.

Figure 1. SEM (a-d) and TEM (e-f) images of GNA, and the schematic illustration of the GNA formation process.

Figure 2. SEM images of SnS₂/GNA-0.5 (a-c), SnS₂/GNA-1 (d-f), and SnS₂/GNA-2 (g-i).

Figure 3. Porosity of neat SnS₂ and SnS₂/GNA-1 by N₂ adsorption-desorption analysis. N₂ adsorption-desorption isotherm at 77 K (a), and pore size distribution as determined by the Barrett-Joyne-Halenda (BJH) method (b).

Figure 4. XRD patterns of GNA, pure SnS₂ and SnS₂/GNA-1, and TGA curves of pure SnS₂ and SnS₂/GNAs.

Figure 5. Cyclic voltammograms of SnS₂/GNA-1 between 0.005 and 3.0 V at a scan rate of 0.1 mV s⁻¹ (a) and discharge-charge profiles of SnS₂/GNA-1 for the 1st, 2nd and 3rd cycles (b).

Figure 6. Rate capabilities of pure SnS₂ (a), SnS₂/GNA-0.5 (b), SnS₂/GNA-1 (c), and SnS₂/GNA-2 (d).

Figure 7. Cycling performances (a), TEM images of SnS₂/GNA-1 after cycling for 50 cycles (b, c), and XRD pattern of SnS₂/GNA-1 on Cu foil after the cycling test (d).

Figure 8. Nyquist plots of GNA, neat SnS₂ and SnS₂/GNAs.

Scheme 1

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Supplementary Materials

[Click here to download Supplementary Materials: Supplementary data.docx](#)

Highly porous nano-aerogels composed of controllable amounts of SnS₂-encapsulated hollow graphene nanoscrolls bridged by wrinkled SnS₂-attached graphene nanosheets are readily synthesized as excellent anode materials for lithium ion batteries.

- Highly porous graphene nanoaerogels with controllable amounts of hollow tubular graphene nanoscrolls bridged by curved graphene nanosheets present an interconnected nanostructure with spacious configuration for confinement of SnS_2 .
- The preparation method is simple and scalable.
- This unique 3D configuration provides spacious inter-space to buffer SnS_2 volumetric expansion/shrinkage and pulverization in cycling tests.
- The SnS_2 /graphene nanoaerogel composite exhibits high reversible capacity and coulombic efficiency, good cycling and rate capability.