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C-Plasma of Hierarchical Graphene Survives SnS Bundles for Ultra-Stable and High Volumetric Na-Ion Storage

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Keywords: Carbon plasma; tin sulfide; hierarchical graphene; alloy anode; battery cycling stability

Abstract: Tin and its derives have provoked tremendous progress of high-capacity sodium ion anode materials. However, achieving high areal, and volumetric capability with maintained long-term stability in a single electrode remains challenging. Here, an elegant and versatile strategy has been developed to significantly extend the lifespan and rate-capability of tin sulfide nanobelt electrode while maintaining high areal and volumetric capacities. In this strategy, in-situ bundles of robust hierarchical graphene (*hG*) are grown uniformly on the tin sulfide nanobelt networks through a rapid (5 min) carbon-plasma method with sustainable oil as the carbon source and the partially reduced Sn as the catalyst. The nucleation of graphene, CN (with size N ranging from 1 to 24), on the Sn(111) surface is systematically explored using density functional theory calculations. We demonstrate that this chemical-bonded *hG* strategy is powerful in enhancing overall electrochemical performance.

Research on the most promising next-generation sodium storage materials, such as tin and its derived materials, has been mostly focused on improvements in the gravimetric capacity. With the increasing demand for miniaturized and portable energy storage devices, high volumetric energy density in limited space becomes a critical parameter. The conventional carbonaceous anodes are limited by their relatively low sodium storage capacity.^[1, 2] Recently, alloying-type anodes, such as Sb nanorod,^[3] SnS nanohoneycomb,^[4] SnO nanosheet,^[5] and branched SnS₂^[6] have been extensively reported to possess enhanced sodium-ion gravimetric, areal, and volumetric storage capacities. But the cycling stability is still a major bottleneck.

Great efforts have been dedicated to improving the cycling stability of the battery electrodes, particularly alloy-type materials. A well-defined conductive network is essential to accommodate the large volume change, stabilize the structure, and supply conductive channels.^[7-9] Current research has shown that the combination of graphene, or more commonly, reduced graphene oxide (rGO), with metal oxides, sulfides, and metal alloys can significantly enhance the sodium storage performance.^[8, 10-14] For instance, Denis Yu *et al.* reported that Sb₂S₃/graphene composite gave a high capacity of 730 mAh g⁻¹ and a stable charge/discharge performance in 50 cycles.^[15] SnS₂/graphene^[16] and SnS/graphene^[17] nanosheets prepared by hydrothermal method with graphene oxide showed a high reversible capacity of 940 mAh g⁻¹ at 0.03 A g⁻¹ with 250 cycles at 7.29 A g⁻¹, and 630 mAh g⁻¹ at 0.2 A g⁻¹ with 400 cycles at 1.0 A g⁻¹, respectively. In another work, SnO₂/SnS/graphene heterostructure^[18] delivered 729 mAh g⁻¹ at 0.03 A g⁻¹ with enhanced cycling stability of 500 cycles at 2.43 A g⁻¹. However, these laminate structures inevitably introduce excess exposure of active materials to the electrolyte, which will form thick solid-state electrolyte interface (SEI), aggregate and detach gradually from the graphene surface. Regrettably, this counters the attempt to obtain long-term cycling life with maintained high-capacity. It remains a big challenge to *in-situ* grow robust graphene onto everywhere of active material nanoarchitectures, especially for the alloying-type electrode materials.

In this work, we develop a facile and rapid C-plasma strategy to *in-situ* generate robust hierarchical graphene bundled onto tin sulfide networks to stabilize its long-cycle capacity for reversible Na-ion storage. This also illustrates that tin is applied as catalyst for the growth of graphene (growth mechanism is supported by density functional theory calculations). In contrast to the conventional laminate graphene composite structure, chemical-bonded hierarchical graphene (*hG*) provides continuous and permanently reliable electric conductivity output. More importantly, this *hG* bundle on the SnS network effectively restricts the active materials re-aggregation and stabilizes the network structure during long-term cycling. As a result, high

volumetric capacity of 1530 mAh cm⁻³ for the whole electrode and unprecedented 1600 cycles at 3 A g⁻¹ with 93% retention are achieved.

Formation Mechanism of CN (N = 1, ..., 24) Clusters on Sn(111). The possible formation mechanism of C clusters on the surface of Sn is analyzed by density functional theory calculations. All structures were optimized using the conjugate gradient method with the Vienna *ab initio* Software Package (VASP) program (detailed calculation provided in the Supporting Information). The strong binding between the carbon clusters CN (N = 1...24) and the Sn(111) reduces the surface formation energy of graphene edge. For CN clusters on Sn terrace, their ground structures can be classified into two categories: (i) one dimensional C chains for $N \leq 8$ and (ii) two dimensional C networks for $N \geq 9$, because the big C ring case is always less stable than the corresponding C chain, which was also proved by Ding et. al. on a Ni(111) terrace.^[19] All the structures in ground state were explored in [Figure 1 and S1](#) with their corresponding formation energies. It is interesting that the ground state structures of the CN networks explored in this study have one to three pentagons. And the energies of the pure hexagonal networks (C10-H) are significantly larger than pentagon (C10-G), as shown in [Figure S1](#). This finding can be explained by the reduced circumference length or number of edge atoms.^[19, 20] By calculation of formation energies (E_{form}) as function of size N of graphene nucleation on Sn(111), we can deduce that when the size of the C cluster is larger than 12, the nuclei will be a stable one due to the significantly reduced E_{form} (see [Figure S2](#)). As illustrated by charge density difference of C24 in [Figure 1](#), interactions between carbon clusters and Sn(111) surface mainly occur inside graphene layer, suggesting very weak interaction between the carbon cluster and the substrate. Different with C8 and C13 ([Figure S2](#)), they present strong interaction to passivate the dangling bonds of the smaller carbon cluster. The results implies that Sn, as the typical alloy-type anode material for metal-ion batteries, is also an efficient catalysis for growth of graphene nanostructures.

Figure 1. Optimized most stable structure for six typical CN ($N = 8, 9, 10, 13, 16, 24$) clusters on the surface of Sn terrace. G represents its ground state, and H is the hexagon-only structure. Their corresponding formation energies and charge density difference for C24 clusters are also given.

Fabrication and Characterization of the *hG@SnS* bundles. The SnS nanobelts were synthesized using a one-step hydrothermal method (see the Supporting Information for more details). As illustrated in [Figure 2A and S3](#), the SnS nanobelts, with lengths of dozens of micrometres, are entangled network to form a free-standing membrane. The SnS nanobelts have a consistent width of ca. 100 nm. After the C-plasma treatment, hierarchical graphene (*hG*) grow uniformly onto the SnS nanobelts ([Figure 2B](#)). The network structure remains same but the connection is further strengthened by the *hG*. This leads to the excellent flexibility of *hG@SnS* bundle membrane which can be demonstrated even after continuous bend ([Figure S4](#)). Typical XRD pattern of pure SnS nanobelts in [Figure 2C](#) can be well indexed to orthorhombic crystalline phase of SnS (Space group: Pnam, JCPDS 39–0354). Two new peaks at 43.8° and 55.3° are found in the diffraction pattern of *hG@SnS*, corresponding to tetragonal Sn (JCPDS 04–0673). That implies that metal Sn are present in the *hG@SnS* bundles, which is a result of hydrocarbon plasma reduction of SnS due to the effective plasma electron impact dissociation of the carbon-based oil. The broad XRD peak at $25\text{--}27^\circ$ belongs to hierarchical graphene in the sample, which was also proved by Raman results in [Figure S5](#).

Figure 2. Structure characterization of *hG@SnS* bundles membrane electrode. A) FESEM images of pure SnS nanobelts and B) *hG@SnS* bundle. Insets: Their low magnification SEM images. C) XRD patterns of pure SnS nanobelts and *hG@SnS* membrane. D) HRTEM image of pure SnS nanobelt. Inset: the corresponding fast Fourier transform (FFT) pattern in the [010] zone axis. E) HRTEM image of hierarchical graphene. Inset: low magnification TEM image of the *hG@SnS* bundles. F) HRTEM image shows a typical interface between hierarchical graphene and SnS.

High-resolution transmission electron microscope (HRTEM) images reveal a typical ribbon morphology with a smooth surface and single-crystallinity for as-synthesized SnS (Figure 2D). Lattice fringes with d-spacings of 0.42, 0.39, and 0.30 nm can be observed in [010] zone axis, corresponding to (100), (001), and (101) planes of SnS, respectively. Inset fast Fourier transform pattern also discloses the nanobelt grows along the [001] direction (shown in Figure S6A-D). The SnS nanobelt turns to be mesoporous after the C-plasma treatment (Figure S6E-G and inset in Figure 2E). The hierarchical graphene displays a lateral size ca. 100 nm, a thickness 2–6 nm, and lattice spacing of 0.36 nm in (002) facets. It is proved that the structure and morphology of C-plasma grown graphene is strongly determined by substrate-plasma species interaction.^[21, 22] Interestingly, the hierarchical graphene exhibits a branched feature (Figure S7), possibly due to the gradually mesoporous catalytic sites of Sn/SnS, floating electric field in the plasma sheath, and formation of mismatched graphitic layers at the surface, leading to growth of irregular and random branched graphene.^[21, 23] The interface between Sn and graphene can be clearly seen (Figure 2F and S8A), where the lattice spacing of 0.29 nm corresponds to the (200) facet of Sn. The thickness

of Sn layer is estimated 3–5 nm, and the Energy-dispersive X-ray (EDX) analysis in [Figure S8B](#) shows even distribution of Sn, S, and C signals with an average atomic ratio of Sn:S ca. 1.2:1.

Na ion storage performance of the *hG*@SnS bundles. The approaches above enable reversible Na^+ storage with bi-continuous electron and Na-ion transfer channels in the electrode material, as shown schematically in [Figure 3](#). We argue that the unique flexible *hG*@SnS bundles membrane configuration can efficiently alleviate the existing problems of tin sulfide electrodes from the following aspects. i) The 3D crosslinked structure with the uniform graphene coating provides a perpetual and continuous electronic conductive network, promoting the electrode reaction kinetics. ii) The *hG* wrapping around the mesoporous SnS together with internal voids efficiently accommodates the volume expansion, relax the strain, and avoids the agglomeration of SnS during the sodiation/desodiation processes (see [Figure S9A-F](#)). This makes the membrane electrode robust and stable. iii) The exposed *hG* can prevent the extensive exposure of active materials to the electrolyte; Instead, a relatively stable SEI layer will form both on the graphene and SnS surfaces, which maintains the electrochemical activity of the active material during long-term cycles as well as the entire nanobelt morphology (see more evidence in [Figure S9 and S10](#)). Last but not the least, this free-standing network membrane does not require the usage of the extra binders, conductive additives or metal Cu current collectors, and thus beneficial to increasing the energy/power densities.

Figure 3. Schematic illustration of three types of electrode configurations and their structural evolutions. A) Pure SnS nanobelts network undergoes substantial volume expansion, induces internal stress, and causes severe pulverization and aggregation. The exposed cracks offer fresh sites for the growth of thick and passivating SEI layer, accounting for conductivity decrease and large irreversible capacity fading. B) rGO/SnS laminate composite film provides a protective cover for SnS with improved electric conductivity. But poor cycling stability are still serious due to free volume expansion, particle detachment from rGO, and gradually deteriorated reaction kinetics. C) Hierarchical graphene bundle serves as a conductive buffering framework, which effectively restricts the reaggregation and thus stabilizes the structure, allowing an ultralong cycle life and high rate performance.

We now present the detailed electrochemical properties of our *hG@SnS* anode and demonstrate its superiority to pure SnS nanobelts and rGO/SnS laminate composites. At a current density of 3 A g⁻¹, the *hG@SnS* bundles and pure SnS nanobelts film present significant difference in their capacity retentions, i.e. 93% after more than 1600 cycles and 19% after only 260 cycles, respectively (Figure 4A). As a comparison, although reduced graphene oxide (rGO) was used to form the rGO/SnS laminate composites (see Figure S9D) and provide the necessary electric contact, limited cycling stability improvement of SnS can be achieved with retention of 68% after 660 cycles due to the decreased conductivity and reaggregation by high volume expansion (Figure 3B and S10C,D). Figure 4B displays their rate performances comparison at rates from 0.2 to 20 A g⁻¹. The pure SnS nanobelts film shows steep capacity decay especially in the initial 5 cycles due to the pulverization followed by particle aggregation (Figure 3A and S10A,B) and electroconductivity loss. The rGO/SnS and *hG@SnS* all present high reversible capacities of 790 and 850 mAh g⁻¹, respectively, at 0.2 A g⁻¹ (Figure 4B). At a relatively high current density of 5 A g⁻¹ *hG@SnS* achieves a high capacity of 585 mAh g⁻¹, which is 1.6 and 6.6 times higher than those of rGO/SnS and pure SnS electrodes, respectively (Figure 4B). Further enhancing the current density to as high as 20 A g⁻¹, 345 mAh g⁻¹ still maintains for *hG@SnS*, more than 8 times than that of rGO/SnS. Note that the pure hierarchical graphene contributed negligibly to the capacity (ca. 40 mAh g⁻¹ at 0.2 A g⁻¹ shown in Figure S11). Electrochemical impedance spectroscopy (EIS) is employed to understand the charge transfer properties on the foregoing electrodes (Figure S12A). The charge transfer resistance R_{ct} of the *hG@SnS* is determined to be ~38 Ω, which is much smaller than that of the pure SnS nanobelts (171 Ω) and rGO/SnS (72 Ω) electrodes, suggesting better electric conductivity and fast electronic mobility in the *hG@SnS* bundles. EIS studies also provided complementary insights to the change in interface state at different cycles (data presented in Figure S12 and Table S1). The *hG@SnS* electrode shows fairly steady charge transfer resistances after 50 cycles and up to 250 cycles, indicating that the SEI layer is stable and of

protective nature. This is also in consistent with the XPS results (see detailed description in [Figure S13](#)). [Figure 4C](#) displays the galvanostatic profiles of the *hG@SnS* after an activation of 4 charge/discharge cycles with first-cycle coulombic efficiency ca. 75% (see [Figure S14A](#)). The voltage profile shows continuous slope charge/discharge curves without obvious plateaus, which is a typical feature of capacitive charge storage behaviour of a battery material.^[4, 24] The degree of capacitive effect can be qualitatively analysed by separating the current response into diffusion-controlled and capacitive contributions^[25]: $i(V) = k_1V + k_2V^{1/2}$ (k_1 and k_2 are constants). Among them, capacitive charge storage has the advantage of rendering high charging rate and therefore high power.^[6, 26] As a result, a 76% dominating capacitive contribution is identified, even at a relatively slow sweep rate of 0.8 mV s⁻¹ when diffusion contributions are maximized (see [Figure S14D and 4D](#)). This is unsurprising since the pseudocapacitive contribution would be multiplied for electrodes with high electric conductivity, thin-sheet, and mesoporous features.^[27-29]

The *hG@SnS* bundles membrane electrode delivers a superior volumetric capacity. The volumetric-specific capacity can reach 1530 mAh cm⁻³ at a current density of 0.2 A g⁻¹ and maintains 620 mAh cm⁻³ at 20 A g⁻¹, on the basis of the total whole volume of SnS and graphene in *hG@SnS* under the state of sodiation. These volumetric capacities are quite high among all the reported sodium alloys, oxides, sulfides and carbonaceous anodes so far (see a comprehensive comparison in [Figure 4E and Table S2](#)).

Finally, we assembled soft-packed pouch cell based on the *hG@SnS* anode and flexible Na₃(VO)₂(PO₄)₂F array cathode to demonstrate the potential application of our *hG@SnS* anode material for full Na-ion batteries (see [Figure S15 and 16](#)). This full cell exhibits a maximum energy density of ~200 Wh kg⁻¹ based on the total mass of the cathode and anode including current collector thanks to the free-standing and binder-free features of both cathode and anode. The cell can retain 87% of initial capacity after 120 cycles. For a proof-of-concept demonstration, the pouch cell can power a rotation motor (3 V, 0.4 W) and fan even under severe bending.

Figure 4. Electrochemical performances of the $hG@SnS$ bundles membrane electrode. A) High-rate long-term cycling stability of SnS electrodes at 3 A g^{-1} . B) Rate performances of pure SnS nanobelts film, rGO/SnS laminate, and $hG@SnS$ bundles electrodes at various current densities from 0.2 to 20 A g^{-1} . C) Galvanostatic charge/discharge profiles and corresponding volumetric capacities at various current densities of $hG@SnS$ bundles electrode after 4 cycles activation at 0.2 A g^{-1} . D) Normalized contribution ratios of capacitive (gray part) and diffusion-controlled (blue) contribution capacities at different scan rates. E) Volumetric capacities comparison with other state-of-the-art reported congeneric sodium ion storage electrode materials and some top performance lithium ion batteries. The volumetric capacities were calculated based on the whole electrode (with mass loading of 4.5 mg cm^{-2} and thickness of $25 \text{ }\mu\text{m}$) including conductive agent. Empty symbols denote to Li-ion electrodes: $t\text{-Si@GN}$,^[30] $SiNP\text{-PANI}$,^[31] $SnO_2@GC$,^[32] Gray symbols are carbonaceous electrodes: $CNT/Mxene$,^[33] pseudographite,^[34] $N\text{-CNF}$,^[35] Folded G ,^[36] Cyan symbols represent metal/alloying electrodes: Sb/rGO ,^[37] Bi/CNF ,^[38] P/rGO ,^[39] P/G ,^[1] Green symbols are other metal oxide/sulfide electrodes: FeS_2/CNT ,^[9] SnS_2/rGO ,^[40] MoS_2/CNT ,^[41] MoS_2/rGO ,^[42] MoS_3 .^[43]

In conclusion, we have achieved ultra-long cycling stability in alloying-type high capacity Na-ion storage materials by using an efficient and effective C-plasma approach to *in-situ* generate hierarchical graphene growth on Sn-based bundles (and also SnS_2 nanowall, see Figure S17). Calculations suggests that the hG growth is catalysed by Sn. With this electrode design, we show high volumetric and areal capacities of 1530 mAh cm^{-3} and 3.82 mAh cm^{-2} , respectively, for the whole electrode with excellent cyclic stability of 93% retention after 1600 cycles at 3 A g^{-1} . Our C-plasma based strategy fulfils most of stringent requirements for balancing the large volume

expansion with high areal and volumetric capacity and the long cycle life of SnS. It could be a universal approach to many Sn-based nanostructured materials in both Na-ion, K-ion, and Li-ion storage.

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TOC entry

Hierarchical graphene bundled Tin Sulfide ($hG@SnS$) was fabricated by ingenious *in-situ* C-plasma route and tested as flexible anode for sodium-ion batteries with unprecedented cycling lifespan and maintained ultrahigh areal and volumetric capacities. DFT calculation verified the formation mechanism of graphene by catalysis of Sn.

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