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Coupling Topological Insulator SnSb₂Te₄ Nanodots with Highly Doped Graphene for High-Rate Energy Storage

Abstract

Topological insulators have spurred worldwide interest, but their advantageous properties have scarcely been explored in terms of electrochemical energy storage, and their high-rate capability and long-term cycling stability still remain a significant challenge to harvest. p-Type topological insulator SnSb₂Te₄ nanodots anchoring on few-layered graphene (SnSb₂Te₄/G) are synthesized as a stable anode for high-rate lithium-ion batteries and potassium-ion batteries through a ball-milling method. These SnSb₂Te₄/G composite electrodes show ultralong cycle lifespan (478 mAh g⁻¹ at 1 A g⁻¹ after 1000 cycles) and excellent rate capability (remaining 373 mAh g⁻¹ even at 10 A g⁻¹) in Li-ion storage owing to the rapid ion transport accelerated by the PN heterojunction, virtual electron highways provided by the conductive topological surface state, and extraordinary pseudocapacitive contribution, whose excellent phase reversibility is confirmed by synchrotron in situ X-ray powder diffraction. Surprisingly, durable lifespan even at practical levels of mass loading (>10 mg cm⁻²) for Li-ion storage and excellent K-ion storage performance are also observed. This work provides new insights for designing high-rate electrode materials by boosting conductive topological surfaces, atomic doping, and the interface interaction.

Keywords

topological, energy, coupling, high-rate, graphene, doped, highly, nanodots, snsb₂te₄, storage, insulator

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Coupling topological insulator SnSb₂Te₄ nanodots with highly doped graphene for high-rate energy storage

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Keywords: topological insulators, SnSb₂Te₄, batteries, high-rate, heterojunction

Abstract

Topological insulators have spurred worldwide interest, but their advantageous properties have scarcely been explored in terms of electrochemical energy storage whose high-rate capability and long-term cycling stability still remain a significant challenge to harvest. Herein, p-type topological insulator SnSb_2Te_4 nanodots anchoring on few-layered graphene ($\text{SnSb}_2\text{Te}_4/\text{G}$) was synthesized as a stable anode for high-rate lithium-ion batteries and potassium-ion batteries by a ball-milling method. The $\text{SnSb}_2\text{Te}_4/\text{G}$ composite electrode shows ultra-long cycle lifespan (478 mAh g^{-1} at 1 A g^{-1} after 1000 cycles) and excellent rate capability (remaining 373 mAh g^{-1} even at 10 A g^{-1}) in Li-ion storage owing to the rapid ion transport accelerated by the PN heterojunction, virtual electron highways provided by the conductive topological surface state, and extraordinary pseudocapacitive contribution, whose excellent phase reversibility was confirmed by synchrotron in situ X-ray powder diffraction. Surprisingly, durable lifespan even at practical levels of mass loading ($>10 \text{ mg cm}^{-2}$) for Li-ion storage and excellent K-ion storage performance were also observed. This work provides new insights for designing high-rate electrode materials by boosting conductive topological surfaces, atomic doping, and the interface interaction.

High-power mechanical and electronic devices require the development of ever faster charging/discharging and higher energy density batteries.^[1] The current Li-ion batteries (LIBs) based on graphite anodes cannot fulfill the increasing demand due to the disadvantage of low specific capacity (theoretically 372 mAh g⁻¹), poor rate performance, and a low voltage platform that easily induces the uncontrolled growth of lithium dendrites at high rates.^[2] New high-rate electrode materials are urgently needed to increase power and decrease charging time of batteries.^[3]

Multinary metal oxides/chalcogenides are attractive for their diverse composition, tunable crystal structure and unique morphologies, endowing them with outstanding physical, chemical, optical and electronic properties.^[4] The possible synergistic effect of the electroactive multi-components makes it promising for electrochemical energy storage applications^[5]. For example, Wang *et al.*^[5] reported that a layered SnSSe anode can deliver high capacity and superior cycling stability for sodium-ion batteries, taking advantage of the expanded interlayer spacing and better electrical conductivity through partial substitution of S by Se. Meanwhile, Jia *et al.*^[6] also reported that ultrathin MoS_{2-x}Se_x nanoflakes growing on the carbon foam presented an improved capacity and rate performance for Na-ion storage via the partial substitution of S by Se. Apart from the reports of mixed anions in multinary chalcogenides, the effect of mixed cations has been reported sparsely. Previously, we summarized NiCo₂O₄ as a promising energy storage material for electrochemical supercapacitors,^[7] owing to its comparable capacitive performance with noble metal oxides of RuO₂, and richer electroactive sites and at least two magnitudes greater electrical conductivity than that of NiO and Co₃O₄.^[8] In addition, we also designed atomically thin Bi₂MoO₆ nanosheets for LIBs with excellent high-rate cycling performance owing to the interlayer coupling effect, the two-dimensional (2D) configuration and intrinsic structural stability. The built-in electrical fields induced by the unbalanced charge distribution can boost lithium ion transfer dynamics while the extra charge transport channels generated on the open surfaces

can promote charge transport.^[9] Most recently, niobium tungsten oxides were highlighted for high-rate lithium-ion energy storage, by virtue of the multielectron redox reaction, rapid solid-state lithium transport, buffered volume expansion, and polyhedral structure, showing even better performance than Nb₂O₅ and Li₄Ti₅O₁₂ for high-power/fast-charging applications.^[3] The excellent electrochemical performances provided by multinary metal chalcogenides and oxides have sparked our research interest in this field. A layered topological insulator SnSb₂Te₄ has attracted our attention recently due to the possible synergetic effects from mixed cations, higher electronic conductivity and larger interlayer spacing provided by Te element when compared with S and Se element,^[10] ultrahigh theoretical volumetric specific capacity of 3702 mAh cm⁻³ (with theoretical mass specific capacity of 565 mAh g⁻¹),^[11] and intrinsic properties of topological insulator (TIs).^[12] The three-dimensional (3D) p-type topological insulator SnSb₂Te₄, with a narrow band gap of 0.32 eV, adopts a hexagonal crystal structure ($R\bar{3}mh$) with seven alternating anion and cation layers in one block separated by van der Waals gaps.^[13] Of particular note is that 3D TIs are a new class of quantum matter that behave as an insulator in its interior but have a gapless metallic state on its surface with non-trivial symmetry-protected topological order, which means that electrons can only transfer freely along the 2D surface of the material.^[12a, 14] In this case, the electrical conductivity of these topological insulators can be modulated upon thinning, since increased exposed 2D surfaces will provide increased “perfect highways”, that are immune to weak disorder or impurities, for electron transport than its bulk counterpart.^[14-15] The breakthrough of 3D TIs in experimental realization and theoretical prediction, including Bi₂Te₃,^[16] Sb₂Te₃^[12b, 17] and SnTe,^[18] has attracted worldwide attention, showing promising applications in magnetoresistive devices,^[19] optoelectronic devices,^[20] spintronics and quantum computation.^[12a] However, as far as we know, the effect of TIs for electrochemical energy storage has not been emphasized and the electrochemical performances of SnSb₂Te₄ electrodes have not been reported to date.

In this work, we pioneered the theoretical analysis of TIs for electrochemical energy storage. 3D TI SnSb_2Te_4 flakes were synthesized by a facile and scalable ball-milling approach, whose structure was identified by synchrotron neutron powder diffraction (NPD) and X-ray powder diffraction (XPRD). After unzipping it with graphite by further ball-milling, the SnSb_2Te_4 nanodots (~ 10 nm) were coupled with few-layered graphene, showing unprecedented high-rate capability and durable cycling performance for pseudocapacitive Li-ion and K-ion storage, by virtue of the formation of the PN heterojunction between the single-atom doped graphene and thin SnSb_2Te_4 nanodots which is highly conductive on its surface with the native topological surface states. Furthermore, we identified the excellent reversibility of $\text{SnSb}_2\text{Te}_4/\text{G}$ composite electrode by *in situ* XPRD, and also investigated the electrochemical process of bare SnSb_2Te_4 electrode in LIBs by combining *ex situ* XPRD and X-ray absorption spectroscopy (XAS). This work presents interdisciplinary research towards advanced composite materials design for electrochemical energy storage, covering synergistic modulation of the dimensionality/composition, atomic doping, TIs, interfaces, and electric field effects.

As described in **Figure 1a**, the $\text{SnSb}_2\text{Te}_4/\text{G}$ composite was prepared by mechanical exfoliation of layered bulk SnSb_2Te_4 flakes and synthetic graphite by a facile and scalable ball-milling method, where the SnSb_2Te_4 nanodots and few-layered graphene sheets are derived from the strong interaction among layered bulk SnSb_2Te_4 , graphite flakes and steel balls triggered by the high shear and fragmentation forces during ball-milling.^[21] The joint refinement of X-ray and neutron powder diffraction data (**Figure 1c** and **d**) reveals that SnSb_2Te_4 adopts a hexagonal $R\bar{3}m$ space-group and consists of repeated septuple layers of mixed Sn/Sb/Te atoms stacking along the c-axis of the unit cell with van der Waals gaps between each group of the septuple layer (**Figure 1b**).^[13b] The crystallographic details of SnSb_2Te_4 are provided in **Table S1**, whilst the X-ray powder diffraction (XPRD) patterns of SnSb_2Te_4 , the $\text{SnSb}_2\text{Te}_4/\text{G}$ composite and graphite are compared in **Figure S1**. X-ray

photoelectron spectroscopy (XPS) confirmed the native oxide layers on the surface of SnSb₂Te₄ (**Figure 1e** and **Figure S2**), which is similar to the phenomenon discovered in SnTe,^[22] Sb₂Te₃^[23] and (Bi_{1-x}Sb_x)₂Te₃.^[24] Surprisingly, SnSb₂Te₄ and the SnSb₂Te₄/G composite display similar spectra in high-resolution Sn 3d spectra and Sb 3d spectra, but are quite different in high-resolution Te 3d spectra, which indicate that the dominated doping could come from the Te element. As shown in **Figure 1e**, the high-resolution Te 3d spectra of SnSb₂Te₄ can be deconvoluted into two pairs of peaks assigned to Te⁴⁺ (575.7 and 586.3 eV) and Te²⁺ (571.9 and 582.5 eV),^[22b] but there is an additional pair of peaks in the SnSb₂Te₄/G composite that can be assigned to be Te-C bond (573.1 and 583.6 eV).^[25] Moreover, the peak of high-resolution C 1s spectrum of the SnSb₂Te₄/G composite in **Figure S2** can be deconvoluted into sp² C=C (284.0 eV), sp³ C-C (284.6 eV), C-O (285.5 eV), C-Te (286.8 eV) and C=O (288.6 eV).^[25] The ratio of Te-C bond on the surface was calculated to be 7.6 %.

Considering that enriched Te doping makes graphene more electron-rich^[26] and that SnSb₂Te₄ belongs to p-type topological insulators,^[13a, 27] the electron clouds are biased from Te-doped graphene to SnSb₂Te₄, leading to a strong electronic coupling between the SnSb₂Te₄ and Te-doped graphene which ensures a stable structure for superior long-term cycling performance in battery applications. Raman spectroscopy was also conducted to identify the structure of carbon materials in the SnSb₂Te₄/G composite (**Figure 1f**). The SnSb₂Te₄/G composite displayed three prominent peaks, including the G band at 1593 cm⁻¹ corresponding to the stretching vibration E_{2g} observed for sp² carbon domains, and the D band at 1332 cm⁻¹ and D' band at 1614 cm⁻¹ attributed to the defect-induced double resonance Raman feature. Besides, it displays weak G' band at ~2642 cm⁻¹ and D+D' band at ~2891 cm⁻¹, originating from the second order of the D peak and the combination of phonons with different momentum around the K and Γ points (activated by defects), respectively.^[28] Compared with pristine synthetic graphite, the composite showed a blue shift of the G band position and a red

shift of the G' band position, revealing the possible change from the graphite crystal to few-layered graphene and the nature of n-type doping of graphene, respectively.^[25, 29] Generally, the intensity ratio of I_D/I_G can be used to estimate the disorder of graphene while the intensity ratio of $I_D/I_{D'}$ can be used to get information on the type of defects in graphene.^[30] The composite shows stronger D-band intensity and remarkably higher ratio of I_D/I_G (2.09) than pristine synthetic graphite (0.26), indicating that the enriched Te-doped graphene sheets with reduced grain size are more disordered than the pristine graphite. The peak intensity of the D' band was almost equal to that of the G band in the composite, and the low ratio of $I_D/I_{D'}$ (2.26) implies the boundary-like defects in graphene.^[30]

As shown in **Figure S3**, bare SnSb_2Te_4 was composed of large stacked flakes and the selected area electron diffraction (SAED) pattern confirmed its polycrystalline nature of the SnSb_2Te_4 sample. The $\text{SnSb}_2\text{Te}_4/\text{G}$ composite (**Figure S4**) was also composed of flakes and the bright-field TEM images reveal that many black nanodots were randomly distributed within the matrix. To further investigate the details of the composite, sub-angstrom-resolution, aberration-corrected scanning transmission electron microscopy (STEM) was used to observe the composite. The STEM images of the composite in **Figure 2a and Figure S5** also reveals that many SnSb_2Te_4 nanodots were randomly distributed within the carbon matrix, and the corresponding EDS mapping of the composite in **Figure S5** shows that the Sn, Sb, and Te elements are uniformly distributed in the graphene matrix with atomic ratio to be 1: 1.97: 4.04. Quadruple-layered graphene was observed in **Figure 2b**, whilst the other magnified bright-field STEM image in **Figure 2e** reveals that the marked carbon layers here consist of bi-layered graphene and the crystalline nanodots (~ 10 nm) with interplanar spacing of 0.32 nm can be indexed into the (107) lattice plane of SnSb_2Te_4 . Furthermore, atomic resolution high-angle annular dark field (HAADF) images were also conducted to study heavy atoms in carbon given its sensitivity to atomic number Z-contrast, as shown in **Figure 2c, f and g**. Obviously, numerous individual atoms were loaded on the edge of graphene (**Figure 2c and**

g), which is consistent with the doping phenomenon detected by Raman and XPS. The corresponding EDS mapping in **Figure 2d** reveals that Sb and Te could be dominated for the doping at the graphene edge, but it is hard to further distinguish their differences in doping concentration under this poor resolution. The HAADF-STEM image in **Figure 2f** reveals that SnSb_2Te_4 nanodots are surrounded by few-layered graphene and they are well-distributed within the few-layered graphene framework, which is favorable for accommodating volume changes during battery cycling. Other representative STEM images in **Figure S6** also show similar characteristic results that the few-layered graphene was highly doped by single atoms on the edge and the SnSb_2Te_4 nanodots (~ 10 nm) were anchored on the graphene layers. The multi-element single-atom doping enables n-type doped graphene that is demonstrated by Raman test, which couples strongly with p-type topological insulator SnSb_2Te_4 .^[13a] More importantly, however, the highly doped graphene at the single-atom level will provide more effective active sites for pseudocapacitive storage. Furthermore, since TIs have a full insulating gap in the bulk and gapless edge or surface states which are protected by time-reversal symmetry, TIs nanodots with large surface areas will endow it with enhanced surface metallic conduction.^[14] These SnSb_2Te_4 nanodots (~ 10 nm) loaded on the graphene will further enhance the conductivity of the composite. The $\text{SnSb}_2\text{Te}_4/\text{G}$ composite has more than one-magnitude higher electrical conductivity than the bare SnSb_2Te_4 material, as observed by four-point probe resistance measurement (**Figure S7**).

The electrochemical performances of the $\text{SnSb}_2\text{Te}_4/\text{G}$ composite and SnSb_2Te_4 as LIB anodes were evaluated in coin-type 2032 cells within a potential window of 0.01 and 2.5 V. The cyclic voltammetry (CV) curves of the initial five cycles of the $\text{SnSb}_2\text{Te}_4/\text{G}$ anode were shown in **Figure 3a**. For simplification, considering SnSb_2Te_4 as the combination of SnTe and Sb_2Te_3 , its electrochemical process can, to a first approximation, be deduced from these two materials.^[31] During the first cathodic scan, the $\text{SnSb}_2\text{Te}_4/\text{G}$ composite electrode exhibits a minor reduction peak at around 1.50 V, originating from the Li^+ intercalation into the layered

SnSb₂Te₄ host. The broad and large peak centred at 1.18 V can be attributed to the conversion reaction to generate Sn, Sb and Li₂Te.^[32] The peak located at 0.83 V should be related to the further lithiation process of Sb to form Li₃Sb,^[33] while two peaks located at 0.14 and 0.50 V should correspond to the multiply lithiation processes of Sn.^[34] During the first anodic scan, the oxidization peaks situated at 0.54 and 0.80 V correspond to the multiple delithiation of Li₂₂Sn₅ to form Sn,^[34] while the peaks at 1.08 and 1.22 V are associated with the multiple delithiation of Li₃Sb to form Sb.^[33] The sharp peak observed at 1.78 V should be related to the conversion reaction among Sn, Sb, and Li₂Te, accompanied by the formation of Li_xSnSb₂Te₄. The minor peak observed 2.09 V should be the extraction of Li⁺ from the host and the formation of SnSb₂Te₄. In the following repeated scans, the oxidization peaks are nearly completely overlapped, and so are the reduction peaks, which reflect highly reversible kinetics in the SnSb₂Te₄/G electrode. It is noted that the peak centered at 1.18 V shifts toward 1.30 V after the initial cycle, which can be ascribed to an activation process in the initial lithiation process or the reduced polarization of the electrode/electrolyte interface after the initial cycle.^[35] A CV measurement was also performed on the bare SnSb₂Te₄ electrode (**Figure S8a**). In comparison, it shows irreversible peaks and shapes in the initial five cycles, which implies a different electrochemical process.^[31b, 36] Additionally, the SnSb₂Te₄/G composite anode delivers an initial discharge capacity of 707 mAh g⁻¹ at 0.1 A g⁻¹ with a high initial coulombic efficiency (CE) of 81.2 %, while the SnSb₂Te₄ anode yields an initial CE of 84.1 % (**Figure 3b and S8b**). Remarkably, the SnSb₂Te₄/G composite electrode exhibited high discharge specific capacities of 574, 527, 503, 481, 455, 414, 373 mAh g⁻¹ at the current density of 0.1, 0.2, 0.5, 1, 2, 5, 10 A g⁻¹, respectively, as shown in **Figure 3c**. It reveals significantly better rate performance than bare SnSb₂Te₄ and graphite anodes, with high rate retention of 65.0 % from 0.1 to 10 A g⁻¹ and a capacity as high as 373 mAh g⁻¹ retained even at 10 A g⁻¹. Surprisingly, its capacity can even recover to 577 mAh g⁻¹ at 0.1 A g⁻¹ (**Figure 3d**). In addition to the excellent rate performance, the SnSb₂Te₄/G electrode also delivers

better cycling stability over bare SnSb_2Te_4 , Sn/C , Sb/C and Te/C electrodes, as shown in **Figure 3e** and **S9**. When cycled at 1 A g^{-1} (**Figure 3e**), the $\text{SnSb}_2\text{Te}_4/\text{G}$ electrode can retain a large reversible capacity of 478 mAh g^{-1} even after 1000 cycles, with high capacity retention of 92.5 %. Interestingly, the Te/C composite electrode also reveals good cycling stability but suffers from low specific capacity, whilst the SnSb_2Te_4 , Sn/C and Sb/C composite electrodes show poor cycling stability despite their relatively higher specific capacities. This work also occupies a leadership at rate capability and cycling stability among SnSb alloys and Te -based materials for LIBs, as shown in **Figure 3f**.^[31a, 37] More strikingly, even at ultra-high mass loading of 11 mg cm^{-2} (**Figure 3g**), the $\text{SnSb}_2\text{Te}_4/\text{G}$ electrode can still last for about 80 cycles with high capacity at the current density of 200 mA g^{-1} , which is critically important for practical applications. The excellent electrochemical performance of the $\text{SnSb}_2\text{Te}_4/\text{G}$ composite can be attributed to strong coupling effect between the SnSb_2Te_4 TI nanodots and highly doped few-layered graphene.

To determine the relationship between rate performance and pseudocapacitive contribution of the $\text{SnSb}_2\text{Te}_4/\text{G}$ electrode in LIBs, we tested a series of CV measurements variable from 0.1 to 1.2 mV s^{-1} for kinetics and quantitative analysis. As plotted in **Figure 3h**, all the CV curves display analogous shapes, with peak current rising gradually along with the increasing scan rates, which indicates a typical pseudocapacitive behavior and excellent high-rate capability. The capacitive contribution can be quantitatively deduced from the equation ($i = mv^n$, both m and n are constants), which describes the relationship between current (i) and scan rate (v) in the CV curves.^[38] A linear relationship between $\log(i)$ and $\log(v)$ can be established based on the equivalent equation, $\log(i) = n \log(v) + \log(m)$, in which the value of n ($0.5 \leq n \leq 1$) is the slope of the $\log(i)$ versus $\log(v)$ plot and relies on the solvated ions storage mechanism ($n=1$ for extreme pseudocapacitive-controlled process while $n=0.5$ for extreme diffusion-controlled process). As shown in **Figure 3i**, the simulated value of n of the five peaks suggests that the

surface pseudocapacitive-controlled Li^+ storage mechanism is dominant in the $\text{SnSb}_2\text{Te}_4/\text{G}$ anode. To be more accurate, we adopted another equation ($i = k_1v + k_2v^{1/2}$, which is equal to $iv^{-1/2} = k_1v^{1/2} + k_2$, k_1 and k_2 are constant) to quantitatively determine the pseudocapacitive (k_1v) and intercalation ($k_2v^{1/2}$) contributions by separating the current response i at a fixed voltage^[5]. As a result, at 0.8 mV s^{-1} , the pseudocapacitive contributions from peak a to peak e are calculated to be 65.9 %, 81.2 %, 98.0 %, 89.4 %, and 73.5 %, respectively. The inset of **Figure 3i** illustrates a separation of the surface pseudocapacitive-controlled current from the entire CV curve at 0.8 mV s^{-1} , with a capacitive contribution of 87 % in total. Moreover, the ratios of pseudocapacitive contribution increases towards higher scan rates (**Figure 3j**).

Electrochemical impedance spectroscopy (EIS) experiment confirms the enhanced electron and Li-ion transport after coupling SnSb_2Te_4 nanodots with few-layered graphene (**Figure 3k**), which was demonstrated by the smaller diameter of semicircle which indicates reduced charge-transfer impedance and the closer inclined line towards 90° which indicates improved Li-ion diffusion observed in the $\text{SnSb}_2\text{Te}_4/\text{G}$ composite electrode, thus enabling excellent high-rate pseudocapacitive performance in the $\text{SnSb}_2\text{Te}_4/\text{G}$ composite electrode.^[39]

The excellent phase reversibility of the $\text{SnSb}_2\text{Te}_4/\text{G}$ composite electrode was confirmed by *in-situ* synchrotron XPRD ($\lambda=0.6887 \text{ \AA}$). The contour plots of the *in situ* data in **Figure 4a** and **b** describes the changing process of (110) peak with $2\theta=18.65^\circ$ and (107) peak with $2\theta=12.57^\circ$ of the $\text{SnSb}_2\text{Te}_4/\text{G}$ composite in the first cycle, respectively. Moreover, the corresponding XRD patterns of $2\theta=12.57^\circ$ were shown in **Figure 4c**. During the discharging process, the (107) and (110) peaks of SnSb_2Te_4 consecutively shift towards lower angle until 1.35 V, suggesting the increase of the lattice parameter due to the intercalation of Li^+ to form the $\text{Li}_x\text{SnSb}_2\text{Te}_4$ phase. Afterward, the peak intensity becomes weaker till almost disappeared. Surprisingly, the peak of $\text{Li}_x\text{SnSb}_2\text{Te}_4$ phase appeared again at ca. 1.5 V upon charging and then continually shifts towards higher angle to form SnSb_2Te_4 . This implies that the $\text{SnSb}_2\text{Te}_4/\text{G}$ composite electrode was reversible and should undergo the typical three-step

insertion/conversion/alloying process upon lithiation and a reversible dealloying/recombination/extraction process upon delithiation, which is consistent with the CV results above. It is noted that the re-merged peak was ~33 % broader than the initial one, indicating that the crystalline size was further reduced after cycling.^[31a] Due to the low degree of crystallization of the $\text{SnSb}_2\text{Te}_4/\text{G}$ composite, the small SnSb_2Te_4 nanodots within the composite and the size-reduced products, synchrotron XPRD cannot tell the full story of the electrochemical mechanism with the composite electrode. *Ex situ* XPRD and X-ray absorption near edge structure (XANES) were conducted to investigate the bare SnSb_2Te_4 electrode at different charge states. The *ex situ* XRPD data in **Figure 4d** confirms the formation of Li_2Te when discharged to 1.0 V (D 1.0 V), as well as the formation of $\text{Li}_{22}\text{Sn}_5$ and Li_3Sb when fully discharged to 0.01 V (D 0.01 V). However, the peaks of Sn and Sb elements were not detected due to their poor intensity in *ex situ* XPRD upon discharging. When charged to 1.0 V (DC 1.0 V), all the peaks nearly overlapped with D 0.01V except that the peak at 23.4° became sharp and narrow. This means that the number of components decreased within this peak, which could come from the fully extraction of $\text{Li}_{22}\text{Sn}_5$ at the point of DC 1.0 V. However, the location of the major peaks of $\text{Li}_{22}\text{Sn}_5$, Li_3Sb and Li_2Te are quite close, making it difficult to distinguish them under the poor resolution. When fully charged to 2.5 V (DC 2.5 V), SnTe were detected, while Sb and Te elements were possibly involved within these broad peaks, revealing that the SnSb_2Te_4 compound was not re-combined any more.

XANES is particularly suited to provide insight into the partial densities of unoccupied states of Sb element so as to identify the charge transfer during lithiation and de-lithiation processes. The edge is interpreted as the electronic transitions to empty states, which are perturbed by the creation of a core-hole.^[40] The *ex situ* XANES data and its corresponding second-derivative normalized spectra based on Sb K-edge (30491 eV) are shown in **Figure 4e** and **f**,

respectively. At the start of the lithiation (D 2.5 V), the white-line of the XANES spectrum is sharp but then broadens as the lithiation proceeds, indicating a decrease of unoccupied 5p electronic states due to the changes of charge transfer. This assumes that the charge transfer from p band of Sb to Te at the point of D 2.5 V results in increased intensity at the white-line, while the charge transfer from Li to Sb at the point of D 0.01 V results in weak intensity at the white-line where Li_3Sb was confirmed by *ex situ* XRPD. It is noted that the white-line peak and the rising edge of D 1 V are nearly overlapped with that of the Sb reference spectra, indicating the possible formation of amorphous Sb at D 1 V undetected by XRPD (above). When delithiated, Li was not extracted from Li_3Sb yet at the point of DC 1 V, revealing nearly overlapped white-line with D 0.01 V, then Li was fully extracted at the point of DC 2.5 V with more intense white-line. Surprisingly, the white-line of DC 2.5 V was lower than that of D 2.5 V, which means that the local environment around the Sb was not recovered at all even after fully charged. The corresponding second-derivate of XANES spectra displayed in **Figure 4f** reveals that the edge (the intercept at the imaginary line) shows almost no shift when discharged to 1 V (breaking the Sb-Te bond into Sb-Sb bond has almost no influence on the edge position), but shifts toward higher energy when further discharged to 0.01 V (breaking Sb-Sb bond into Li-Sb bond). Upon charging, the edge position reveals almost no shift when it was charged to 1 V since Li was not extracted from Li_3Sb at this point, and then shifts back to lower energy when fully charged to 2.5 V as Li was fully extracted. These trends are fingerprinted by the standardized reference samples in **Figure S10**, where the edge position should be in the order of $\text{Sb}_2\text{O}_3 > \text{Sb}_2\text{S}_3 > \text{Sb}_2\text{Se}_3 > \text{Sb} > \text{Sb}_2\text{Te}_3$, among which the edges of Sb and Sb_2Te_3 are quite close. It is also identified that the edge position of Li_3Sb was at higher energy when compared with Sb-reference.

Given the chemical similarity between K^+ and Li^+ , we also evaluated the electrochemical performances of the $\text{SnSb}_2\text{Te}_4/\text{G}$ composite toward PIB application. As shown in **Figure 5a**

and b, the $\text{SnSb}_2\text{Te}_4/\text{G}$ electrode delivers discharge specific capacity of 450, 368, 325, 289, 255, 215, 153 mAh g^{-1} at different current densities of 0.05, 0.1, 0.2, 0.5, 1, 2, 5 A g^{-1} , respectively, manifesting an outstanding high-rate capability in 1 M KFSI/DMC electrolyte. More importantly, the $\text{SnSb}_2\text{Te}_4/\text{G}$ electrode (**Figure 5c** and **S11**) also shows a long-term cycling lifespan at either large or small current density, delivering high capacity retention of 91.2 % over 200 cycles at 500 mA g^{-1} and 84.3 % over 180 cycles at 100 mA g^{-1} in 1M KFSI/DMC electrolyte. According to a previous study by our group,^[41] potassium bis(fluorosulfonyl)imide (KFSI) salt has shown an advantage over KPF_6 salt in suppressing the growth of potassium dendrites and reducing the effect of polarization. Based on the KFSI salt, we further investigated the effects of different solvents on the cycling stability of the electrode in PIBs. Three types of solvents were compared, including dimethyl carbonate (DMC), diethyl carbonate (DEC) and ethylene carbonate (EC) / DEC ($v/v=1/1$). As shown in **Figure 5c**, the $\text{SnSb}_2\text{Te}_4/\text{G}$ electrode using KFSI/DMC electrolyte cycles stably at 500 mA g^{-1} over 200 cycles, but the electrode using KFSI/EC/DEC electrolyte cycles stably for merely 140 cycles. Unfortunately, the electrode using KFSI/DEC electrolyte is unable to complete the first cycle, due to the serve reduction of DEC by K metal from breaking the $\text{C}(\text{H}_2)\text{--O}$ bond in the solvent molecule.^[42] It is clear from the inset in **Figure 5d** that the K metal immersed in KFSI/DEC electrolyte is black, in sharp contrast with the colors observed in freshly sheared K metal (silver), the K metal immersed in KFSI/DMC (silver) and KFSI/EC/DEC electrolyte (light blue). These results suggest a completely different reactivity between the K metal and electrolytes, highlighting that DMC should be a highly compatible solvent for PIBs. The advanced KFSI/DMC electrolyte enables the $\text{SnSb}_2\text{Te}_4/\text{G}$ electrode with a relatively high initial CE of 77.9 % and a stable CE as high as ca. 99.3 % at 500 mA g^{-1} over 200 cycles. In order to further study the effects of electrolytes on polarization and potassium dendrite growth, symmetric potassium foil cells were assembled with different electrolytes. **Figure 5d** describes the voltage profiles of symmetric potassium foil cells using the

KFSI/DMC and KFSI/EC/DEC electrolyte over 500 h at 1 mA cm^{-2} , and the K//K cell using KFSI/DMC electrolyte delivered a lower electrode overpotential for K metal stripping/plating ($\pm 100 \text{ mV}$) than the cell using KFSI/EC/DEC electrolyte ($\pm 200 \text{ mV}$). It is noted that the symmetric potassium foil cells based on KFSI/DEC electrolyte failed to work. The decrease of the overpotential in the first tens of cycles should be ascribed to the gradually reduced interfacial resistance and the more stable solid electrolyte interface (SEI) being established at the surface of the potassium metal electrode upon cycling.^[43] More intriguingly, we obtained ultra-long cycling performance over 1000 cycles at 100 mA g^{-1} in graphite anode using KFSI/DMC electrolyte, in spite of the poor rate performance of the graphite anode in PIBs (**Figure S12**). In conclusion, these results demonstrate that KFSI/DMC electrolyte can be an excellent electrolyte to suppress the dendrite growth in K metal stripping/plating kinetics, thus enabling outstanding cycling performance in PIBs. The excellent rate and cycling performance of the $\text{SnSb}_2\text{Te}_4/\text{G}$ composite used as anodes for PIBs were comparable with other reported work recently (**Figure 5e**).^[44] The surface pseudocapacitive contribution of the $\text{SnSb}_2\text{Te}_4/\text{G}$ anode in PIBs was also quantitatively analyzed, which occupies a relatively high ratio of 66.3 % for the total charge storage at a scan rate of 0.8 mV s^{-1} (the inset of **Figure 5g**), according to the CV curves in **Figure 5f** using the equations mentioned in the part of LIBs. At 0.1, 0.2, 0.4, 0.8 and 1.2 mV s^{-1} , the pseudocapacitive contributions (**Figure 5h**) of $\text{SnSb}_2\text{Te}_4/\text{G}$ were calculated to be 51.7 %, 55.9 %, 61.8 %, 66.3 % and 76.1 %, respectively, which were even more prominent than that from hollow carbon nanospheres for PIBs,^[45] though not to the level of LIBs presented herein.

Based on the above results, a possible mechanism for the excellent lithium/potassium storage in the $\text{SnSb}_2\text{Te}_4/\text{G}$ composite could be proposed in **Figure 6**. Firstly, the highly doped few-layered graphene enables ultrafast surface pseudocapacitance at the single-atom heavy metal active reaction centers and 2D few-layered graphene surface. It not only enables ultrafast

Li^+/K^+ ion conductivity, but also provides robust buffer layers to accommodate volume expansion for long-term cycling stability.^[46] Secondly, the SnSb_2Te_4 nanodots can provide abundant exposed conductive topological surfaces to transfer electrons efficiently, and the Te anion can provide much larger interlayer than S and Se anions for the insertion/extraction of alkali metal ions. It is noted that there is a two-dimensional limit for SnSb_2Te_4 being a 3D TIs upon thinning, since thickness-dependent gap will be opened up when the boundary modes from the opposite surfaces are coupled by quantum tunneling. To maintain the unique property of 3D TIs, the two-dimensional thickness of TI SnSb_2Te_4 should not be less than 2 septuple layers (one septuple layer $\approx 13.9 \text{ \AA}$). Therefore, this critical thickness ($\approx 2.8 \text{ nm}$) can be the optimal thickness to take full advantage of the topological metallic surface states.^[47] Upon thinning beyond the two-dimensional limit, more topological conductive surfaces are exposed, which facilitates to enhance electronic conductivity and shorten the ion transport path. Lastly, the strong coupling effect between the SnSb_2Te_4 and graphene can build a local electric field to further accelerate the ion transport at the interface, thus boosting the charge transfer process. More importantly, the ion conductivity at the interface is directional transport under the local electric field, which is very important for boosting the performance of thick electrodes.^[48]

With the great advantages above, the $\text{SnSb}_2\text{Te}_4/\text{G}$ composite exhibits a high capacity (574 mAh g^{-1} at 0.1 A g^{-1}), ultralong cycle lifespan (478 mAh g^{-1} at 1 A g^{-1} after 1000 cycles) and excellent rate capability (remaining as high as 373 mAh g^{-1} even at 10 A g^{-1}) for Li-ion storage. By optimizing the electrolyte, the composite electrode also delivers excellent K-ion storage capability, with a capacity retention of 91.2 % over 200 cycles at 500 mA g^{-1} and stable CE approaching 99.3 % in KFSI/DMC electrolyte. These results demonstrate that the $\text{SnSb}_2\text{Te}_4/\text{G}$ composite could be practical and highly functioning anodes for both LIBs and

PIBs for future energy storage requiring high-rate capability by boosting conductive topological surfaces, atomic doping, and the interface interaction.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Figure 1 (a) Schematic illustration of the ball-milling-driven exfoliation and doping process to form the $\text{SnSb}_2\text{Te}_4/\text{G}$ composite; (b) Crystal structure of SnSb_2Te_4 ; Rietveld refinement profiles for (c) NPD and (d) XPRD data of SnSb_2Te_4 with combined goodness-of-fit (GOF) of 1.39 and weighted profile R-factor (R_{wp}) of 3.48 %; (e) High-resolution Te 3d XPS patterns of SnSb_2Te_4 and the $\text{SnSb}_2\text{Te}_4/\text{G}$ composite; (f) Raman spectrum of the $\text{SnSb}_2\text{Te}_4/\text{G}$ composite and synthetic graphite.

Figure 2 Bright-field STEM images (a, b, e and h) and HAADF-STEM images (c, f and g) of the $\text{SnSb}_2\text{Te}_4/\text{G}$ composite in different magnification times; (d) The corresponding EDS mapping of the $\text{SnSb}_2\text{Te}_4/\text{G}$ composite in Figure 2c.

Figure 3 (a) CV curves of the $\text{SnSb}_2\text{Te}_4/\text{G}$ electrode for LIBs measured at 0.1 mV s^{-1} and (b and c) its galvanostatic charge–discharge profiles measured at 100 mA g^{-1} for the initial 2 cycles and at different current densities ranging from 0.1 to 10 A g^{-1} , respectively; (d) Comparison of the rate capabilities of the $\text{SnSb}_2\text{Te}_4/\text{G}$ composite, SnSb_2Te_4 and graphite and (e) the cycling performance of the $\text{SnSb}_2\text{Te}_4/\text{G}$ composite, SnSb_2Te_4 , Sn/C , Sb/C and Te/C at 1 A g^{-1} ; (f) A comparison of cycling and rate performances of the $\text{SnSb}_2\text{Te}_4/\text{G}$ composite with those recent published works in LIBs; (g) Cycling performance of the $\text{SnSb}_2\text{Te}_4/\text{G}$ composite at 200 mA g^{-1} with different mass loading; (h) CV curves of the $\text{SnSb}_2\text{Te}_4/\text{G}$ electrode at different scan rates from 0.1 to 1.2 mV s^{-1} ; (i) Linear relation of $\log(i, \text{peak current})$ and $\log(v, \text{scan rate})$ about peaks of a–e; the inset shows the capacitive (pink) and diffusion-controlled contribution to Li-ion storage at the scan rate of 0.8 mV s^{-1} ; (j) The ratio of capacitive (pink) and diffusion-controlled contribution to Li-ion storage *versus* scan rate; (k) EIS curves of the $\text{SnSb}_2\text{Te}_4/\text{G}$ composite and SnSb_2Te_4 electrode before cycling.

Figure 4 (a and b) Contour plots of *in situ* synchrotron XPRD with superimposed voltage profiles for selected 2θ ranges of the SnSb₂Te₄/G anode for LIBs; (c) Selected ranges of *in situ* XPRD patterns centered at $2\theta = 12.57^\circ$; (d) *Ex situ* XPRD tests of the bare SnSb₂Te₄ electrodes at different cut-off voltages; (e and f) Normalized Sb K-edge XANES spectra and their corresponding normalized second derivative spectra of the *ex situ* SnSb₂Te₄ electrodes at different cut-off voltages, respectively. D stands for discharge and C stands for charge.

Figure 5 (a) Rate capability and (b) its corresponding galvanostatic charge–discharge profiles of the $\text{SnSb}_2\text{Te}_4/\text{G}$ electrode for PIBs measured at different current densities ranging from 0.05 to 5 A g^{-1} in KFSI/DMC electrolyte; (c) Cycling performance of the $\text{SnSb}_2\text{Te}_4/\text{G}$ electrode for PIBs measured at 500 mA g^{-1} with different electrolytes; (d) Galvanostatic cycling of symmetric foil cells in different electrolytes at a current density of 1 mA cm^{-2} with a stripping/plating capacity of 1 mAh cm^{-2} . Insets: detailed voltage profiles for the corresponding times and the digital photos of K immersed in different electrolytes; (e) A comparison of cycling and rate performances of the $\text{SnSb}_2\text{Te}_4/\text{G}$ composite with those recent published works in PIBs; (f) CV curves of the $\text{SnSb}_2\text{Te}_4/\text{G}$ electrode for PIBs measured at different scan rates from 0.1 to 1.2 mV s^{-1} ; (g) Linear relation of $\log(i, \text{peak current})$ and $\log(v, \text{scan rate})$ about peaks of a-e; the inset shows the capacitive (pink) and diffusion-controlled contribution to K-ion storage at the scan rate of 0.8 mV s^{-1} ; (h) the ratio of capacitive (pink) and diffusion-controlled contribution to K-ion storage *versus* scan rate.

Figure 6 Summary of the high-rate lithium/potassium storage mechanism of the $\text{SnSb}_2\text{Te}_4/\text{G}$ composite. (a) Schematic diagram of the robust coupled heterostructures between SnSb_2Te_4 nanodots and graphene; (b) The relationship between the interface electric field and the Li^+/K^+ transport kinetic in the $\text{SnSb}_2\text{Te}_4/\text{G}$ composite; (c) The increase of conductive topological surfaces of TI SnSb_2Te_4 from bulk to nano.

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Topological insulator SnSb_2Te_4 nanodots coupled with few-layered graphene show excellent rate capability and durable cycling performance for pseudocapacitive Li-ion and K-ion storage by boosting the conductive topological surfaces, atomic doping, and the interface interaction, benefitting from the rapid ion transport accelerated by the PN heterojunction, virtual electron highways provided by the conductive topological surface state, and extraordinary pseudocapacitive contribution.

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Coupling topological insulator SnSb_2Te_4 nanodots with highly doped graphene for high-rate energy storage