Branch-structured Bi$_2$S$_3$–CNT hybrids with improved lithium storage capability†

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Bismuth sulfide (Bi$_2$S$_3$) is a promising Li-storage material due to its high gravimetric and volumetric capacities. However, this intrinsic merit has often been compromised by the poor cycle and rate capability due to the lack of structural integrity upon the Li insertion/extraction process. Here, we engineer a branch-structured bismuth sulfide–carbon nanotube (CNT) hybrid by growing Bi$_2$S$_3$ nanorods onto CNTs to mitigate this issue. The hierarchical Bi$_2$S$_3$–CNT hybrids possess high surface areas, rich porosity for electrolyte infiltration, and direct electron transport pathways, and can be employed as efficient electrode materials for Li storage. These electrochemical results show that the Bi$_2$S$_3$–CNT hybrid exhibits a high reversible capacity (671 mA h g$^{-1}$ at 120 mA g$^{-1}$), stable cycling retention (534 mA h g$^{-1}$ after 90 cycles), and remarkable rate capability (399 mA h g$^{-1}$ at 3000 mA g$^{-1}$), notably outperforming other reported Bi$_2$S$_3$ materials. Such superb Li storage capabilities suggest that the Bi$_2$S$_3$–CNT branches could be potential electrodes for rechargeable batteries.

1 Introduction

Increasing concerns on depletion of fossil fuels and environmental pollution lead to a desire to use renewable energy such as solar and wind energies. However, the intermittent characteristics of such renewable energies present tremendous challenges, and thus demand elaborate integration with energy storage systems (ESSs). Amongst currently available ESSs, the Li-ion battery is surely one of the most promising systems due to its high energy density, great flexibility, and environmental benignity. Despite ongoing advancement, current Li-ion batteries are limited by the performance challenges of electrode materials in terms of low energy and power density. To meet the ever-growing demand for higher energy, it is essential to utilize high-capacity anode materials such as metal oxides and sulfides to replace graphite. Through distinct conversion and/or alloying mechanisms, these compounds could afford a capacity up to 600–1000 mA h g$^{-1}$ substantially beyond that of their graphite counterpart (372 mA h g$^{-1}$).

Among the chalcogenides for Li storage, bismuth sulfides (Bi$_2$S$_3$) have attracted growing attention in recent years. Featuring a direct band gap of 1.3 eV, Bi$_2$S$_3$ has been well explored as an important type of semiconductor for versatile applications such as optics, magnetics, biology and energy generation. Specifically, Bi$_2$S$_3$ is regarded as an ideal host for hydrogen storage and lithium storage, owing to its unique laminar structure. In contrast to many other metal chalcogenides such as Fe$_2$O$_3$ and MoS$_2$ (ref. 22) that store Li mainly through a conversion reaction, Bi$_2$S$_3$ storing Li involves successive conversion and alloying processes with a maximum Li uptake of 6.25 Li per unit formula of Bi$_2$S$_3$. This leads to theoretical capacities of 625 mA h g$^{-1}$ by mass or ~4250 mA h cm$^{-3}$ by volume, which are 70% or 420% greater than those of current graphite, respectively.

However, Bi$_2$S$_3$ materials often suffer from unstable performance associated with the poor conductivity and structural integrity induced by huge volume expansion upon Li cycling, which severely compromises their potential in advanced Li-ion batteries. For instance, Ma et al.16 reported that uniform Bi$_3$S$_4$ fibers could deliver 1083 mA h g$^{-1}$ initially but only retained 366 mA h g$^{-1}$ after 10 cycles. Jin et al. also demonstrated that flower-like Bi$_3$S$_4$ retained a low capacity of 169 mA h g$^{-1}$ after 30 cycles. To address this challenge, researchers engineered many Bi$_3$S$_4$ composites. Jung et al. fabricated fine Bi$_3$S$_4$–carbon nanocomposites that retained ~490 mA h g$^{-1}$ for Bi$_3$S$_4$ alone over 100 cycles. However, the excessive carbon (30 wt%) in the composite presents a significant challenge for real application.
Zhang et al. demonstrated that the Bi$_2$S$_3$–RGO (reduced graphene oxide) achieved a capacity of 400.5 mA h g$^{-1}$ over 50 cycles.\textsuperscript{21} Previously, we reported that the carbon coated Bi$_2$S$_3$ nanomeshes demonstrated 472 mA h g$^{-1}$ at 120 mA g$^{-1}$ over 50 cycles, and retained 301 mA h g$^{-1}$ at 600 mA g$^{-1}$ over 40 cycles.\textsuperscript{24} However, both the cycling and rate capability still need further improvement to meet the stringent performance requirement for practical applications.

In this work, we demonstrate the synthesis and Li storage capability of a bismuth sulfide–carbon nanotube (CNT) branched hybrid (denoted as Bi$_2$S$_3$–CNT). This hybrid is fabricated via a facile sonochemical approach followed by crystallization in dimethyl formamide (DMF). The hierarchical Bi$_2$S$_3$–CNT hybrid exhibits unique structural features such as high surface areas, rich porosity, intrinsic flexibility, and direct electron transport pathways. These features ensure rapid electron and ion movement and stable structural integrity upon Li cycling (Fig. 1).\textsuperscript{25} As a consequence, the Bi$_2$S$_3$–CNT hybrids display enhanced Li-storage performance outperforming previously reported Bi$_2$S$_3$ materials.

2 Experimental

2.1 Sample preparation

The synthesis of the Bi$_2$S$_3$–CNT hybrid involves sonochemical hydrolysis of Bi(NO$_3$)$_3$ in the presence of thioacetamide (TAA) and CNTs. In a typical operation, 20 mg HNO$_3$-treated CNTs (Shenzhen Nanoport, 20–30 nm in diameter) were dispersed in 40 mL aqueous solution containing 75 mg TAA (Sinopharm Chemicals) by sonication. To this mixture 5 mL of 0.4 M HNO$_3$ solution containing 0.243 g Bi(NO$_3$)$_3$·5H$_2$O was slowly added, and the suspension was further agitated for 1 hour. The resultant precipitation was then dispersed in 20 mL DMF and solvothermally treated at 150 °C for 2 hours. A free Bi$_2$S$_3$ sample was also prepared via the identical route without CNTs.

![Fig. 1 Schematic illustration of electron and ion transport in the Bi$_2$S$_3$–CNT branched structure.](image-url)

2.2 Characterization

The Bi$_2$S$_3$–CNT samples were characterized by X-ray diffraction (XRD, Rigaku Dmax-2400 automatic diffractometer), scanning electron microscopy (SEM, Hitachi S-4800), transmission electron microscopy (TEM, FEI Teenai G2 T20), Fourier transform infrared spectroscopy (FTIR, Bruker Tensor 27), thermogravimetry and differential thermal analysis (TG-DTA, Seko TG/DTA-7300), and nitrogen adsorption and desorption (Micromeritics Tristar 3202).

The electrochemical Li storage performance of the Bi$_2$S$_3$–CNT was evaluated by coin-type 2032 cells using composite electrodes consisting of 70% active material, 20% Super-P-Li carbon black, and 10% polyvinylidene fluoride binder. The typical loading of the active material was 1.0–1.5 mg cm$^{-2}$. Cells were assembled in an Ar-filled glove box (MBraun) with both water and oxygen concentrations below 1 ppm. The counter and reference electrode are Li metal foil, the electrolyte is 1 M LiPF$_6$ solution in ethylene carbonate and dimethyl carbonate (1 : 1 by volume), and the separator is the Celgard 2320 membrane. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were performed on a Zennium electrochemical workstation (Zahner). Galvanostatic charge and discharge tests were performed on a LAND battery test system (jinnuo) at room temperature.

3 Results and discussion

Morphologies of the Bi$_2$S$_3$–CNT hybrid were observed by SEM and TEM, and the images are illustrated in Fig. 2. The Bi$_2$S$_3$–CNT hybrid after sonochemical reaction shows a branched structure, where the CNT backbones are decorated with numerous Bi$_2$S$_3$ nanorods (Fig. 2a). The Bi$_2$S$_3$ branches are uniform and pretty dense, as clearly shown by the TEM image (Fig. 2c). A high-resolution TEM image of Bi$_2$S$_3$ nanorods shown in Fig. 2d reveals clear lattice fringe spacings of 0.51 and 0.40 nm, corresponding to (120) and (001) facets of orthorhombic Bi$_2$S$_3$, respectively. The (001) plane is perpendicular to the elongation direction of the nanorod, suggesting that each rod is grown along the [010] direction.\textsuperscript{13,24} However, at this stage, the Bi$_2$S$_3$ is still in poorly crystalline state and shows certain structure disorder, as pointed out by the circles in Fig. 2d. Additionally, the lattice fringe of 0.34 nm that corresponds to (002) graphene planes confirms the presence of the CNT backbone.

After solvothermal reaction in DMF, the branched structure is well preserved (Fig. 2b). Nonetheless, the density of Bi$_2$S$_3$ nanorods is slightly reduced (Fig. 2e and f), suggesting that some Bi$_2$S$_3$ rods may be detached from CNTs in DMF. It is noted that the use of aprotic solvents is critical to maintaining the branched structure, otherwise most Bi$_2$S$_3$ rods will detach CNTs if protic solvents such as water or ethanol are employed. The Bi$_2$S$_3$ nanorods are 5–10 nm in width and 30–80 nm in length, and their growth direction is roughly perpendicular to the side surfaces of CNTs to minimize the lattice mismatch at heterojunction interfaces.\textsuperscript{24} The high-resolution TEM image confirms that the crystallinity of Bi$_2$S$_3$ rods is much improved after the
The structure of the Bi$_2$S$_3$–CNT hybrid was identified by XRD, as shown in Fig. 3a. The diffraction peaks in the pattern can be indexed to an orthorhombic Bi$_2$S$_3$ phase (PDF#17-0320),[28] while the (002) peak of CNTs is barely visible, possibly being masked by the surface Bi$_2$S$_3$ phase. The structure of the Bi$_2$S$_3$–CNT was further characterized by FTIR spectroscopy (Fig. 3b). The bands at 1713 and 1633 cm$^{-1}$ are due to C=O and C=C stretching modes, respectively. The peak at 1385 cm$^{-1}$ is assigned to C–OH stretching vibrations, while the peaks in the range of 1124–1025 cm$^{-1}$ are due to C–O vibrations.[29] Besides these bands associated with CNTs, additional bands at 620 and 517 cm$^{-1}$ might be attributed to C–S and O–Bi, respectively, confirming the anchoring of Bi and S species onto CNTs. The band shift of C=O from 1728 to 1713 cm$^{-1}$ also suggests possible charge transfer between functional CNT and Bi$_2$S$_3$.

DMF solvothermal process (Fig. 2g). In the absence of CNTs, the obtained Bi$_2$S$_3$ sample exhibits a spherical morphology with a particle size of about 400 nm (Fig. S1 in the ESI†). The microsphere is actually composed of numerous Bi$_2$S$_3$ nanorods, consistent with Zhang’s report.[27] Energy dispersive spectroscopy (EDS) shown in Fig. 1h reveals that the Bi$_2$S$_3$–CNT hybrid is composed of Bi, S, and C elements.

The Li storage performance of the Bi$_2$S$_3$–CNT was electrochemically evaluated by CV and galvanostatic tests. Fig. 4a shows the CV profiles of the Bi$_2$S$_3$–CNT upon initial three cycles at 0.1 mV s$^{-1}$, which reveal a high and stable reversibility of the hybrid towards the Li reaction. The cathodic peaks at 1.79 and 1.70 V are due to the conversion reaction, where Bi$_2$S$_3$ is reduced to metallic Bi and Li$_2$S. The peaks at 0.70 and 0.59 V may be ascribed to the alloying process, where LiBi and Li$_3$Bi are formed sequentially. Compared with previous Bi$_2$S$_3$ nanomaterials, the Bi$_2$S$_3$–CNT hybrid shows an appreciable peak shift towards higher potential, suggesting reduced polarization.[24] In the reverse process, the dealloying of Li$_3$Bi occurs at 0.97 V, while the recovery of Bi$_2$S$_3$ at 1.83 and 2.11 V.[15] As the anodic peak of the conversion reaction is much weaker than the cathodic one, a substantial portion of Bi$_2$S$_3$ cannot be recovered and contribute to the irreversible capacity loss. An extra redox pair at 2.04/2.35 V may be associated with Li adsorption/desorption in oxygen groups of CNTs, which is generally less reversible.

Galvanostatic curves of the Bi$_2$S$_3$–CNT are presented in Fig. 4b. In the voltage window of 0.01–3.0 V, the initial
rates of 120, 300, 600, and 3000 mA g⁻¹ indicates that the Bi₂S₃ is capable of delivering capacities of 671, 585, 527, and 399 mA h g⁻¹, respectively. The actual capacity of Bi₂S₃ would be 775 and 710 mA h g⁻¹ at a fast sweep rate of 2.0 mV s⁻¹. Even at a fast sweep rate of 2.0 mV s⁻¹, the Bi₂S₃ retains the basic CV profile, suggesting that the electrochemical Li storage in the hybrid has barely been limited by the transport of electrons and Li ions. In addition, the galvanostatic performance further confirms that the Bi₂S₃-CNT has high-rate capability (Fig. 3d). At identical charge-discharge rates of 120, 300, 600, and 3000 mA g⁻¹, the Bi₂S₃-CNT is capable of delivering capacities of 671, 585, 527, and 399 mA h g⁻¹, respectively (taking the 2nd cycle value at each rate). The capacity delivery is also stable for 10 cycles at each rate. At an extremely high rate of 6000 mA g⁻¹, the Bi₂S₃-CNT hybrid still affords 264 mA h g⁻¹. In contrast, the free Bi₂S₃ microspheres only deliver capacities of 385 mA h g⁻¹ at 600 mA g⁻¹ and 250 mA h g⁻¹ at 2000 mA g⁻¹ (Fig. S2b in the ESI†). More importantly, when the rate is decreased, the capacity of the Bi₂S₃-CNT increases accordingly, and a high value of 534 mA h g⁻¹ is recovered at the 90th cycle at 120 mA g⁻¹. These results indicate that the Bi₂S₃-CNT branches significantly outperform versatile reported Bi₂S₃ nanostructures¹⁵,¹⁶,¹⁸,²⁴ and Bi₁₀S₇–CNT thermometer and Bi₂S₃–RGO³⁴ nanocomposites. It is also worth noting that the Li storage performance of such hybrids is comparable or even superior to some well-known sulfide composites such as SnS₂–CNT¹⁰ and MoS₂–CNT,³¹ suggesting the great potential of such branched materials.

Fig. 4e compares the EIS of the Bi₂S₃–CNT electrodes before and after 90 cycles. Both spectra are composed of two semicircles in the high and middle frequencies, and a spike in the low frequency. The interception at the Z_real axis refers to R_s, including solution resistance and contact resistance. The high- and middle-frequency semicircles reflect the interphase resistance (R_i) and charge transfer resistance (R_ct), respectively.³²,³³ It is clearly seen that the Bi₂S₃–CNT electrodes exhibit little variation in the spectroscopy profile after 90 cycles, implying a marked stability. This stability ensures more active material particles participating in the Li storage process, resulting in a higher level of capacity.³⁴

Such an excellent Li storage capability can be correlated with the unique branched structure of the Bi₂S₃–CNT, in which the fine Bi₂S₃ branches tightly anchored on the CNT backbone. The Bi₂S₃ nanorods, 5–10 nm in width and 30–80 nm in length, drastically reduce the diffusion length of electrons and Li ions and ensure their rapid transport.³⁰,³¹ The CNT backbone serves as a flexible and express path for rapid charge transfer and thus lowers the electrode reaction resistance.⁻¹⁵,⁻³⁶ In addition, the CNT could efficiently hold cracked Bi₂S₃ particles during Li cycling and thus minimize their break of electrical contacts with the current collector. Similar phenomena have also been reported for graphene supported nanomaterials.⁻³⁷,⁻³⁸ Moreover, the branched structure allows free penetration of the electrolyte into the bottom of Bi₂S₃ rods and thus avoids depletion of Li ions. Furthermore, the Bi₂S₃–CNT branches are intrinsically flexible, which can efficiently reduce mechanical stress and strain of the electrode upon lithiation and delithiation, thereby warranting maximum electrode stability. As a consequence, the Bi₂S₃-CNT branches exhibit a robust and stable electrochemical behavior towards Li storage.

4 Conclusions

A branch-structured Bi₂S₃–CNT hybrid was readily prepared by a facile sonochemical approach followed by solvothermal crystallization at 150 °C for 2 h. The Bi₂S₃–CNT hybrid is composed of uniform Bi₂S₃ nanorods, 5–10 nm in width and 50–100 nm in length, growing roughly perpendicular to the flexible CNT backbone. This unique Bi₂S₃–CNT hybrid can be employed as an ideal material for electrochemical Li storage. The galvanostatic test results show that the Bi₂S₃–CNT demonstrates high...
reversible capacity (671 mA h g⁻¹), robust rate capability (399 mA h g⁻¹ at 3000 mA g⁻¹), and stable cyclability (534 mA h g⁻¹ after 90 cycles at various rates). Therefore, this work provides a facile approach to fabricate branched structures to improve the Li storage performance of Bi₂S₃ electrodes. Due to its simplicity and efficiency, this approach is intrinsically extendable and tuneable to engineering other chalcogenide materials.

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Notes and references