

Nano Mn/SnS anchored on exfoliated graphite for high-capacity lithium-ion battery anode

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Abstract

SnS is a high theoretical capacity anode material for lithium-ion batteries (LIBs); however, its application is hindered by poor cycling performance. The fabrication of SnS-based composites not only prolongs the discharge/charge cycle life but also enhances the utilization efficiency of tin and sulfur. Herein, a Mn/SnS/graphite multicomponent composite (Mn/SnS-G) for LIB anode is constructed by the high-energy ball milling method. After high-energy ball milling, SnS is pulverized into an amorphous form, while Mn is ground into two crystalline phases. The reversible capacities of the Mn/SnS-G electrode reach 736.7, 680.2, 663.3, 505.4, 494.8, 457.2, 380.8, 385.9, and 382.1 mAh g⁻¹ at current densities of 0.1, 0.2, 0.5, 1, 2, 4, 6, 8, and 10 Ag⁻¹, respectively. After the current density is restored from 10.0 A g⁻¹ to 0.1 A g⁻¹, the capacity is rapidly recovered to 656.5 mAh g⁻¹. This work demonstrates that the lithium storage performance of SnS can be effectively enhanced by incorporating a transition metal. In this configuration, the SnS grains are in close contact with Mn, wherein Mn not only provides localized electrical conductivity but also serves as a buffer to accommodate the volume changes of SnS during discharge/charge cycling. This research provides valuable insights and references for the development of analogous anode materials for LIBs.

1. Introduction

In recent years, with the rapid development of renewable energy, the importance of large-scale energy storage technologies has become increasingly prominent. LIBs have been established as mainstream technologies in the energy storage field owing to their high energy densities. Graphite, widely employed as an anode material in commercial LIBs, exhibits a reversible capacity that is fundamentally constrained to no more than 370 mAh g⁻¹ [1–3]. Given the ongoing trend toward higher performance and increasing diversification of electronic products, there is an urgent need to enhance battery performance by improving the anode properties. SnS-based anodes represent an emerging class of LIB anode materials that offer the advantage of high theoretical capacity. However, the intrinsically low electrical conductivity and the substantial volume expansion and contraction occurring during the discharge/charge process hinder their practical application [4–7].

To enhance the electrical conductivity of SnS-based anode materials, it is essential to introduce a high-conductivity secondary phase to achieve a uniform dispersion of SnS [8]. Graphite, a low-cost material with good electrical conductivity and intrinsic lithium-storage activity, serves as a suitable matrix for dispersing SnS [9]. However, simple mixing of graphite with SnS results in poor dispersion due to the low specific surface area of graphite. A mechanochemical process can effectively exfoliate graphite into graphene. Although the conductivity of graphene is somewhat lower than that of graphite, it remains substantially higher than that of SnS. Moreover, ball milling SnS with graphite not only promotes the exfoliation of graphite into graphene but also pulverizes and exfoliates SnS, converting it into an amorphous phase. By virtue of its lower density relative to that of crystalline SnS, amorphous SnS experiences considerably less volume change over the course of discharge/charge cycling when utilized as an LIB anode [10]. Even when nanosized SnS is uniformly dispersed on well-exfoliated graphene

sheets, the SnS tends to recrystallize into large particles upon repeated cycling, leading to rapid capacity fading. The introduction of a third phase can effectively suppress the agglomeration of SnS. Mn, a transition metal with low environmental impact that can be integrated into the SnS/graphite matrix via mechanical ball milling, results in the uniform spatial distribution of Mn species among the nanosized SnS domains [11, 12]. With the Mn/SnS composite anchored onto the surface of fully exfoliated graphene sheets, this architecture holds great promise for high-performance LIB anodes.

In this study, a facile and scalable one-step high-energy ball milling process was employed to systematically synthesize three categories of materials: pristine SnS, SnS-G, and Mn/SnS-G composites with Mn: SnS molar ratios of 1:1, 2:1, 3:1, and 4:1. Experimental results reveal that the Mn/SnS-G composite with a Mn: SnS molar ratio of 3:1 exhibits superior reversible capacity and cycling stability compared to both pristine SnS and SnS-G. The pulverization and uniform dispersion of SnS lead to substantially enhanced utilization of SnS. Compared with most conventional methods for preparing transition metal-SnS-carbon composites, the approach adopted in this work is simple, rapid, and amenable to scalable, short-time production. This work offers valuable insights and serves as a reference for the development of advanced anode materials for LIBs and electrode materials for other energy storage systems.

2. Experimental Section

2.1 Material Synthesis

SnS, Mn, and graphite powders were purchased from Shanghai Macklin Biochemical Co., Ltd. Mn and SnS powders were mixed at molar ratios of 1:1, 2:1, 3:1, and 4:1. The total mass of each mixed powder was 1.50 g. The mixture was placed into a 50 mL stainless steel vessel; stainless steel balls with diameters of 10 mm, 8 mm, and 5 mm were added in quantities of 5, 10, and 30, respectively. Ball milling was then performed at 900 rpm for 10 hours under an argon atmosphere. The products were denoted as $n\text{Mn/SnS}$, where $n = 1, 2, 3, 4$. In addition, graphite, Mn, and SnS were mixed such that the Mn: SnS molar ratios were 1:1, 2:1, 3:1, and 4:1, with the mass fraction of graphite fixed at 15% of the total mass; then the same ball milling procedure was applied, and the obtained products were labeled as $n\text{Mn/SnS-G}$. As a control experiment, SnS-G was prepared via ball milling, also with a graphite mass fraction of 15%.

2.2 Material Characterization

The crystal structure of the materials was analyzed by X-ray diffraction (XRD, Rigaku Ultima IV, Cu K_α radiation, $\lambda = 1.5406 \text{ \AA}$). The microstructure and morphology of the samples were observed using scanning electron microscopy (SEM, Nova 200 NanoSEM) and transmission electron microscopy (TEM, JEOL JEM-2100F). The surface elemental composition and chemical states of the materials were analyzed by X-ray photoelectron spectroscopy (XPS, PHI 5000, Al K_α radiation).

The active material, acetylene black, and sodium carboxymethyl cellulose were mixed in an 8:1:1 weight ratio. After addition of deionized water, the blend was ground for about 30 min to produce a uniform

slurry. The slurry was uniformly coated onto a copper foil using a doctor blade, and the coating thickness was controlled at 50 μm . The foil was dried in a vacuum oven at 60°C for 12 hours. The dried foil was cut into circular electrode disks of 12 mm diameter using a disk cutter. The cut electrode disks were transferred into an argon-filled glovebox for battery assembly. CR2032 coin-type cells were assembled in an argon-filled glovebox (H_2O and $\text{O}_2 < 0.1$ ppm). A metallic lithium disk was used as the counter electrode, and the electrolyte consisted of 1 mol/L LiPF_6 dissolved in ethylene carbonate/dimethyl carbonate/ethyl methyl carbonate (volume ratio 1:1:1) with 5 wt% fluoroethylene carbonate as an additive. A Celgard 2300 polypropylene membrane was used as the separator. Galvanostatic discharge/charge tests were performed using a LAND battery testing system within a voltage window of 0.01 ~ 3.0 V. Cyclic voltammetry (CV) was conducted on an EC-100X electrochemical workstation at a scan rate of 0.1 mV s^{-1} .

2.3 Theoretical Calculations

First-principles calculations were carried out using the Vienna Ab initio Simulation Package (VASP) based on density functional theory. The projector-augmented wave method and the Perdew–Burke–Ernzerhof generalized gradient approximation functional were employed [13, 14]. Models of the Mn/SnS heterointerface, the SnS surface, and the 3Mn/SnS-G composite were constructed. To unravel the atomic-scale origins of the enhanced material performance, charge density difference analyses were conducted [15].

3. Results and Discussion

XRD measurements were performed to probe the phase of the composite material derived from high-energy mechanical milling. Fig. S1 shows the XRD patterns of SnS, SnS-G, and 1Mn/SnS-G. SnS exhibits a crystalline structure, whereas SnS-G is amorphous. Following the incorporation of Mn, the resulting 1Mn/SnS-G composite remains predominantly amorphous. Figure 1a shows the XRD patterns of 2Mn/SnS-G, 3Mn/SnS-G, and 4Mn/SnS-G. The standard cards of Mn (PDF#97-004-2774) and SnS (PDF#97-042-0954) are listed for reference. No sharp characteristic peaks attributable to SnS were observed in the patterns of the three samples; the original SnS diffraction peaks disappeared and were replaced by broad, diffuse humps, indicating that after high-energy ball milling at 900 rpm for 10 h, the SnS lattice was sufficiently destroyed, its long-range ordered structure was disrupted, and SnS was transformed into an amorphous state [16, 17]. Diffraction peaks matching the Mn standard card were still clearly detected, demonstrating that Mn remained a well-crystallized phase after ball milling. Upon increasing the Mn: SnS molar ratio from 2:1 to 4:1, a monotonic increase in the relative intensities of the Mn-associated diffraction peaks was observed, which correlates with the rising Mn loading in the composites. In addition, no strong sharp peak attributable to graphite was observed; only a weak broad hump appeared, indicating that the added 15 wt% graphite was exfoliated into amorphous carbon [18].

A preliminary evaluation of lithium storage performance was first conducted at a current density of 2 A g^{-1} for 2Mn/SnS-G, 3Mn/SnS-G, and 4Mn/SnS-G to identify the optimal Mn: SnS ratio. The corresponding

discharge/charge cycling performance is presented in Fig. S2. Evidently, 3Mn/SnS-G delivers superior reversible capacity and cycling stability compared to both 2Mn/SnS-G and 4Mn/SnS-G. Based on this result, the best-performing 3Mn/SnS-G and its reference counterparts were further investigated to elucidate the electronic valence states of each element in the materials. Fig. S3 displays the XPS spectrum of SnS, calibrated to the C 1s reference at 284.8 eV. The Sn 3d_{3/2} and Sn 3d_{5/2} peaks appear at 495.5 eV and 486.6 eV, respectively, and the S 2p_{3/2} and S 2p_{1/2} peaks at 162.5 eV and 161.3 eV. The XPS survey of 3Mn/SnS-G and SnS-G is shown in Fig. 1b. Signals of Sn 3d, Sn 3p, Mn 2p, O 1s, C 1s, S 2p, and S 2s were clearly identified in 3Mn/SnS-G, indicating that this composite material is mainly composed of five elements. In contrast, no Mn signal was detected in the reference SnS-G. The O 1s peak in the spectra was mainly attributed to slight surface oxidation and adsorbed oxygen [19].

Figure 1c is the high-resolution C 1s spectra. In both samples, the most intense peak appears at 284.8 eV, which is assignable to C–C/C = C species and originates from the sp²/sp³ hybridized carbon framework of the added graphite and amorphous carbon. This peak was used as the internal reference for charge correction of the binding energies. Figure 1d presents the high-resolution S 2p spectra, which were split by spin–orbit coupling into the S 2p_{3/2} and S 2p_{1/2} doublets. For the SnS-G, the S 2p_{3/2} and S 2p_{1/2} were located at approximately 164.1 eV and 169.4 eV, whereas for 3Mn/SnS-G they were observed at approximately 164.0 eV and 168.8 eV. The lower binding energy peak is assigned to S²⁻ in the Sn-S bond, while the peak at about 168 ~ 169 eV corresponds to S-O species [20, 21]. After the introduction of Mn, the oxidized sulfur peak shifted from 169.4 eV to 168.8 eV, indicating that Mn alters the local electronic environment of sulfur. The high-resolution Sn 3d spectra in Fig. 1e further corroborate the above interaction. For the SnS-G, the Sn 3d_{5/2} and Sn 3d_{3/2} were located at approximately 487.5 eV and 495.9 eV, while for 3Mn/SnS-G the corresponding peaks shifted negatively to about 486.8 eV and 495.1 eV, *i.e.*, an overall shift of about 0.7 eV toward lower binding energy. The lower binding energy of Sn reflects an enhanced electron density in its vicinity, consistent with electron donation from Mn to Sn. This finding attests to the intimate interfacial connectivity and substantial electronic interaction between the Mn species and the SnS grains. Figure 1f depicts the high-resolution Mn 2p spectrum acquired for 3Mn/SnS-G. Two principal signals are discernible at binding energies of approximately 641.2 and 653.4 eV, corresponding to the Mn 2p_{3/2} and Mn 2p_{1/2} levels, respectively. The observed spin-orbit splitting of *ca.* 12.2 eV is consistent with the presence of Mn in an oxidized form [22]. Combined with the crystalline Mn detected by XRD of Fig. 1a, it can be concluded that Mn coexists in the composite material as metallic/low-valence Mn and a surface-oxidized species; the crystalline Mn provides electrical conductivity and volume buffering, while the small amount of surface-oxidized Mn arises from unavoidable slight oxidation during preparation.

The collective XRD and XPS results substantiate that the composite material contains Sn, S, Mn, C, and O, with Mn being successfully integrated into the host matrix. The synergistic negative shifts of the Sn 3d and S 2p characteristic peaks after Mn introduction collectively reveal a significant electronic interaction between Mn and SnS. This interaction, together with the unique phase combination of “amorphous SnS and crystalline Mn”, mutually corroborates that Mn can serve both as a conductive phase providing local

electron transport pathways and as a buffering component to alleviate the volume change of SnS during charge/discharge processes, thereby laying the chemical and structural foundation for the excellent lithium-storage performance of 3Mn/SnS-G.

The morphology and structural features of the Mn/SnS-G and SnS-G composites were examined by SEM and TEM. As shown in Fig. 2a, the SEM image of SnS-G exhibits a pronounced layered stacked structure. After the introduction of Mn, a fundamental change in the morphology of the resulting Mn/SnS-G composite (Fig. 2b) was observed: the layered morphology is replaced by densely packed, uniformly sized nanoparticles uniformly immobilized on the crumpled graphene sheets. This rough yet dense structure effectively prevents the aggregation of Mn/SnS nanoparticles during discharge/charge cycling.

Next, the microstructure of the Mn/SnS-G composite was investigated by TEM (Fig. 2c). A large number of uniformly sized ca. 100 nm Mn/SnS nanoparticles are closely anchored to the surface of transparent, wrinkled graphene sheets. The intimate interfacial architecture established between the components serves a dual function: it facilitates rapid charge transport and effectively cushions the mechanical strain arising from volume fluctuations of the active material over extended cycling. This synergistic structural configuration collectively underpins the markedly improved electrochemical performance of the composite. Figure 2d shows a high-resolution TEM image of Mn/SnS-G, where clear lattice fringes are observed. Lattice spacings of 2.11 Å and 2.92 Å are measured, corresponding to the (1 1 0) plane of Mn and the (2 0 0) plane of Sn, respectively. This finding confirms the simultaneous presence of Sn⁰ and Mn⁰ nanocrystalline phases within the Mn/SnS-G composite. As shown in Fig. 2e, the SAED pattern of Mn/SnS-G exhibits distinct concentric diffraction rings, which are characteristic of a polycrystalline or nanocrystalline structure. The elemental distribution within the composite is further revealed by the mapping images displayed in Fig. 2f. The uniform distribution of Mn, Sn, S, and C is observed, further confirming the nanoscale uniformity and intimate connection between Mn/SnS and graphene. On this basis, it is demonstrated that a well-defined nanostructured Mn/SnS-G electrode has been successfully fabricated, in which composite particles composed of Sn⁰ and Mn⁰ nanocrystals are uniformly and firmly loaded onto a three-dimensional conductive graphene network.

Figure 3a shows the long-term cycling performance of the 3Mn/SnS-G, SnS-G, and pristine SnS at a current density of 0.2 A g⁻¹. The 3Mn/SnS-G delivers an initial discharge capacity of 790 mAh g⁻¹ with an initial Coulombic efficiency (CE) of 85%. The capacity exhibits a marginal rise during the first ~ 25 cycles, which is attributable to an electrochemical activation process. Thereafter, the capacity rises steadily, reaching 765 mAh g⁻¹ at the 260th cycle. The CE increases rapidly and subsequently stabilizes above 99.5%, reflecting highly reversible lithium storage. In contrast, the SnS-G electrode exhibits an initial capacity of 400 mAh g⁻¹ and an initial CE of 75%, but its capacity fades quickly with considerable CE fluctuation. The pristine SnS electrode delivers only 175 mAh g⁻¹ with an initial CE of 60%, suggesting severe structural degradation upon cycling.

Figure 3b compares the long-term cycling performance of the three electrodes at a high current density of 4 A g⁻¹. The 3Mn/SnS-G electrode exhibits the best cycling stability, delivering an initial capacity of

approximately 330 mAh g⁻¹ and maintaining a capacity retention of 85% after 100 cycles, with the CE remaining stable above 99%. In comparison, the SnS-G electrode delivers an initial capacity of about 290 mAh g⁻¹ but experiences pronounced capacity decay upon cycling, while the SnS fades rapidly to nearly zero. These results further demonstrate that the synergistic effect of Mn incorporation and graphite compositing effectively preserves structural stability even under extreme discharge/charge conditions, thereby enabling the potential application of this material in high-power scenarios.

Figure 3c compares the rate performance of the 3Mn/SnS-G, SnS-G, and SnS electrodes at various current densities. The 3Mn/SnS-G electrode exhibits the best rate capability, delivering reversible capacities of 736.7, 680.2, 663.3, 505.4, 494.8, 457.2, 380.8, 385.9, and 382.1 mAh g⁻¹ at current densities of 0.1, 0.2, 0.5, 1.0, 2.0, 4.0, 6.0, 8.0, and 10.0 A g⁻¹, respectively. Upon returning the current density from 10.0 to 0.1 A g⁻¹, the capacity promptly recovers to 656.5 mAh g⁻¹, corresponding to a recovery ratio of as high as 97.3%. The SnS-G electrode delivers considerably lower capacities at all rates, with values of 588.4, 548.6, 494.8, 439.9, 362.4, 284.9, 237.3, 168.2, and 107.1 mAh g⁻¹ recorded from 0.1 to 10.0 A g⁻¹. When the current density is returned to 0.1 A g⁻¹, the capacity recovers to 569.7 mAh g⁻¹, yielding a recovery ratio of approximately 97.2%. This suggests that graphite compositing improves the reversibility of the material to a certain degree. The SnS electrode exhibits the poorest rate performance, with pronounced capacity fluctuations across all rates. Figure 3d compares the rate performance of the 3Mn/SnS-G electrode with those of recently reported SnS-based and SnS₂-based anode materials for LIBs. The 3Mn/SnS-G electrode consistently affords higher reversible capacities than its counterparts over the entire current density range, underscoring its superior rate capability [23–31].

To elucidate the lithium storage mechanism, the electrochemical behavior of the SnS-G and 3Mn/SnS-G electrodes was investigated. Figure 4a presents the CV curves of the SnS-G electrode recorded at a scan rate of 0.1 mV s⁻¹ within a voltage window of 0.0 ~ 3.0 V for five cycles. Given the considerable irreversible capacity observed in the initial cycle, the subsequent analysis of the lithium storage mechanism is based on the second through fifth cycles, over which the discharge/charge profiles are largely coincident. For the SnS-G, reduction peaks are observed at 1.12–1.17 V, ~ 0.45 V, 0.25 V, and 0.17 V. The peak at 1.12–1.17 V corresponds to the conversion reaction of SnS with Li to form Sn and Li₂S. The peaks at ~ 0.45, 0.25, and 0.17 V correspond to the multi-step alloying reaction of Sn with Li, ultimately forming Li_{4.4}Sn. The intermediate phases include Li₂Sn₅, LiSn, Li₇Sn₃, Li₁₃Sn₅, and Li₇Sn₂, collectively denoted as Li_xSn (x ≤ 4.4). In the anodic scan, oxidation peaks appear at 0.50–0.54 V, 1.23 ~ 1.26 V, and 1.90 V. The peak at 0.50 ~ 0.54 V is attributed to the dealloying of Li_xSn into Sn and Li. The peak at 1.23 ~ 1.26 V corresponds to the reaction of Sn with Li₂S to form Li_ySnS (y > 0), and the peak at 1.90 V is assigned to the complete delithiation of Li_ySnS back to SnS. Figure 4b displays the CV curves of the 3Mn/SnS-G electrode. The redox peak positions are nearly identical to those of the SnS-G electrode, albeit with broader peaks. Notably, no distinct redox peak is observed near 1.9 V, indicating that the reconversion reaction of Li₂S and Sn to Li⁺ and SnS is completed at 1.35 ~ 1.36 V. This suggests that Mn incorporation enhances the reversibility of the reaction between SnS and lithium.

Figure 4c and 4d present the galvanostatic discharge/charge profiles of the SnS-G and 3Mn/SnS-G electrodes. Both SnS-G and 3Mn/SnS-G exhibit well-preserved galvanostatic profiles from 0.1 to 10 A g⁻¹, demonstrating superior rate capability. Notably, the 3Mn/SnS-G electrode delivers a higher reversible capacity than the SnS-G electrode, indicating that Mn incorporation improves the utilization of SnS.

Surface pseudocapacitive analysis was performed to probe the fast Li⁺ diffusion kinetics within the electrode. Figures 5a and 5b show the CV curves of the 3Mn/SnS-G and SnS-G electrodes acquired at scan rates of 0.2 ~ 1.0 mV s⁻¹. The redox peak currents for both electrodes increase progressively with increasing scan rate. Based on the power-law relationship described in Text S1, the logarithm of the peak current was plotted against the logarithm of the scan rate, as shown in Fig. 5c and 5d. The *b*-values derived from these plots are approximately 0.9 for both electrodes, indicating that the electrochemical reactions of 3Mn/SnS-G and SnS-G are predominantly governed by surface-capacitive processes. For comparison, the CV curves of pristine SnS at various scan rates and the corresponding log *I*_p versus log *v* plot are presented in Fig. S4a and S4b, respectively. The *b*-value obtained for pristine SnS is significantly below 0.8, indicative of slower lithium reaction kinetics compared to its counterparts [29, 30, 32, 33].

The pseudocapacitive contributions of the 3Mn/SnS-G and SnS-G electrodes at various scan rates were further quantified and summarized in Fig. 5e. Across the entire scan rate range, the pseudocapacitive contribution of 3Mn/SnS-G increases markedly from 61.5% to 82.8%, reflecting a predominantly surface-controlled charge storage mechanism. In contrast, the pseudocapacitive contribution of SnS-G remains consistently below 30%, indicating that its charge storage is still largely governed by sluggish bulk diffusion processes. Under all conditions examined, the pseudocapacitive contribution of 3Mn/SnS-G far exceeds that of SnS-G. As illustrated in Fig. 5f, at a scan rate of 1.0 mV s⁻¹, the pseudocapacitive contribution of 3Mn/SnS-G reaches 82.8%, highlighting the highly active surface nature of the 3Mn/SnS-G electrode.

To further evaluate the lithium-ion diffusion kinetics, GITT measurements were performed on the 3Mn/SnS-G and SnS-G electrodes, as shown in Fig. 5g. The Li⁺ diffusion coefficients (*D*_{Li⁺}) were calculated according to the procedure described Text S2, and the results are presented in Fig. 5h and 5i. As shown therein, the *D*_{Li⁺} values of 3Mn/SnS-G are approximately one order of magnitude higher than those of SnS-G during both charging and discharging processes. This observation corroborates the synergistic effect of Mn doping and the conductive framework in enhancing electronic conductivity and promoting Li⁺ migration.

To further elucidate the microstructural evolution mechanisms of the different electrode materials during long-term cycling, SEM characterization was performed on the 3Mn/SnS-G, SnS-G, and pristine SnS electrodes at different cycling stages at a current density of 4.0 A g⁻¹. Figure 6a, 6d, and 6g present the surface morphologies of the pristine 3Mn/SnS-G, SnS-G, and SnS electrodes; no obvious cracks are observed on any of the three pristine electrodes. Figure 6b, 6e, and 6h display the electrode surfaces after 200 discharge/charge cycles at 4.0 A g⁻¹. The 3Mn/SnS-G electrode remains free of noticeable cracks, whereas both the SnS-G and SnS electrodes exhibit distinct cracking, with the cracks on the SnS

electrode being larger than those on the SnS-G electrode. Figure 6c, 6f, and 6i show the electrode surfaces after 400 cycles at the same current density. Collectively, these observations demonstrate that the 3Mn/SnS-G electrode affords substantially superior structural stability over extended cycling as compared to the SnS-G and unmodified SnS electrodes.

To probe the interfacial interactions and charge transfer between Mn, SnS, and graphite at the atomic level, DFT-based charge density difference analysis was conducted. Three model systems were examined: Mn/SnS-G, Mn/SnS, and SnS-G. The results are presented in Fig. 7. In these maps, yellow regions represent electron enrichment, while cyan regions indicate electron loss. From these maps, both the direction and the extent of electron redistribution at the interfaces can be directly visualized.

As shown in Fig. 7a, significant charge redistribution occurs near the contact interfaces among Mn, SnS, and graphite in the Mn/SnS-G. Charge depletion appears predominantly around the Mn atoms, whereas noticeable charge accumulation is observed on the adjacent SnS and graphite sides. This distribution indicates that electrons are transferred from Mn to SnS and graphite. It further confirms that Mn donates electrons to the SnS side and that a strong electronic interaction exists between them. This interfacial charge redistribution establishes a fast electron transport pathway between Mn and SnS, thereby enhancing the local electronic conductivity of the composite. Additionally, the incorporation of graphite creates a continuous percolating conductive network across the entire composite, which further expands the charge transfer region and reinforces the overall electronic connectivity. For comparison, Fig. 7b shows that strong charge transfer and redistribution are also observed at the Mn-SnS interface in the Mn/SnS. This finding suggests that the intrinsic electronic interaction between Mn and SnS is the primary source of the improved conductivity. In the absence of graphite, however, the charge redistribution is predominantly confined to the Mn-SnS interface, thereby precluding the establishment of a continuous charge percolation pathway over extended length scales. In marked contrast, the SnS-G system manifests only feeble charge redistribution at the SnS-graphite interface. Both the charge accumulation and depletion regions are limited in extent, indicating that the electronic interaction arising solely from the contact between SnS and graphite is weak and that the degree of electron transfer is restricted. Comparison among the three models confirms that Mn introduction is the dominant factor responsible for strong interfacial charge transfer, with graphite serving to extend and reinforce the conductive network. The most pronounced charge redistribution, generated by the synergistic interaction among Mn, SnS, and graphite in the Mn/SnS-G, theoretically substantiates the following mechanism: Mn not only functions as a conductive phase that provides local electron transport pathways but also stabilizes the SnS structure through electronic interaction. This mechanism is consistent with the excellent electrical conductivity, rate capability, and cycling stability observed experimentally for this composite material, collectively accounting for the intrinsic origin of its enhanced lithium storage performance.

To evaluate the stability of Mn atoms on the SnS-G composite substrate, their binding energy was calculated according to $E_b = E_{\text{Mn/SnS-G}} - (E_{\text{Mn}} + E_{\text{SnS}} + E_{\text{G}})$ [34]. The E_b was determined to be - 0.71 eV, indicating the Mn atoms interact with both the SnS and graphite components via strong chemical

bonding rather than weak van der Waals interactions. Such strong binding effectively anchors the Mn atoms, thereby preventing their migration or agglomeration during cycling. Furthermore, it reinforces the interfacial adhesion between SnS and graphite, which provides a crucial thermodynamic guarantee for the structural robustness of the electrode, thereby accounting for its superior capacity retention upon prolonged cycling.

4. Conclusion

In this study, a series of Mn/SnS-G multiphase composite materials were successfully synthesized via the high-energy ball milling method, and the optimal Mn-to-SnS molar ratio was determined to be 3:1 through systematic compositional optimization. When employed as an anode for LIBs, the optimized 3Mn/SnS-G delivers a high reversible capacity of 663.3 mAh g⁻¹ at 0.5 A g⁻¹ and delivers 500 mAh g⁻¹ after 500 cycles at 2 A g⁻¹. Material characterization and theoretical calculations confirm that Mn-SnS nanoheterojunctions are intimately coupled with a graphite network, and strongly coupled heterointerfaces between Mn and SnS induce interfacial charge redistribution and enhance electronic conductivity. Concurrently, the graphite matrix constructs a continuous flexible conductive framework that effectively disperses the active particles and accommodates the volume expansion during discharge/charge cycling. The synergistic effect of these two components significantly accelerates lithium-ion diffusion kinetics, suppresses electrode pulverization and crack propagation, and ultimately endows the material with high capacity, superior rate capability, and long-term cycling stability. Consequently, the intrinsic drawbacks of SnS anodes are effectively mitigated. This work provides a new strategy and experimental foundation for the rational design and scalable fabrication of high-performance anode materials for lithium-ion batteries.

Declarations

Notes: The authors declare no competing financial interest.

Availability of Data: The raw data supporting the conclusions of this article will be made available by the corresponding author on request.

Author contributions: T.B. Zeng designed the project, performed the experiment; Z.H. Qiu performed and analyzed the experimental data, and the theoretical calculations; Y. H. Ding guided the use of partial instruments; T.B. Zeng and Z.H. Qiu co-wrote and revised the manuscript; All authors discussed the results and commented on the manuscript.

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References

1. C.-M. Park, J.-H. Kim, H. Kim, H.-J. Sohn, Li-alloy based anode materials for Li secondary batteries. *Chem. Soc. Rev.* **39**(8), 3115–3141 (2010)
2. M. Li, J. Lu, Z. Chen, K. Amine, 30 Years of Lithium-Ion Batteries. *Adv. Mater.* **30**(33), 1800561 (2018)
3. T. Kim, W. Song, D.-Y. Son, L.K. Ono, Y. Qi, Lithium-ion batteries: outlook on present, future, and hybridized technologies. *J. Mater. Chem. A* **7**(7), 2942–2964 (2019)
4. M. Kim, J. Cho, Reversible and High-Capacity Nanostructured Electrode Materials for Li-Ion Batteries. *Adv. Funct. Mater.* **19**(10), 1497–1514 (2009)
5. U. Sonapatel, K.N. Nandeesh, K. Prashantha, Recent advances on metal sulfides as next-generation electrodes for supercapacitor energy storage: A holistic review. *Next Mater.* **9**, 101103 (2025)
6. A. Glibo, N. Eshraghi, Y. Surace, A. Mautner, H. Flandorfer, D.M. Cupid, Comparative study of electrochemical properties of SnS and SnS₂ as anode materials in lithium-ion batteries. *Electrochim. Acta.* **441**, 141725 (2023)
7. J. Xia, K. Jiang, J. Xie, S. Guo, L. Liu, Y. Zhang, X. Wang, Tin disulfide embedded in N-, S-doped carbon nanofibers as anode material for sodium-ion batteries. *Chem. Eng. J.* **359**, 1244–1251 (2019)
8. A.R. Kamali, D.J. Fray, Tin-based materials as advanced anode materials for lithium ion batteries: A review. *Rev. Adv. Mater. Sci.* **27**, 14–24 (2011)
9. X. Wang, L. Fan, D. Gong, J. Zhu, Q. Zhang, B. Lu, Core–Shell Ge@Graphene@TiO₂ Nanofibers as a High-Capacity and Cycle-Stable Anode for Lithium and Sodium Ion Battery. *Adv. Funct. Mater.* **26**(7), 1104–1111 (2016)
10. W. Li, S. Hu, X. Luo, Z. Li, X. Sun, M. Li, F. Liu, Y. Yu, Confined Amorphous Red Phosphorus in MOF-Derived N-Doped Microporous Carbon as a Superior Anode for Sodium-Ion Battery. *Adv. Mater.* **29**(16), 1605820 (2017)
11. H. Zhang, H. Zhao, M.A. Khan, W. Zou, J. Xu, L. Zhang, J. Zhang, Recent progress in advanced electrode materials, separators and electrolytes for lithium batteries. *J. Mater. Chem. A* **6**(42), 20564–20620 (2018)
12. Y. Wang, Y. Zhang, J. Shi, X. Kong, X. Cao, S. Liang, G. Cao, A. Pan, Tin sulfide nanoparticles embedded in sulfur and nitrogen dual-doped mesoporous carbon fibers as high-performance anodes with battery-capacitive sodium storage. *Energy Storage Mater.* **18**, 366–374 (2019)
13. M. Ernzerhof, G.E. Scuseria, Assessment of the Perdew-Burke-Ernzerhof exchange-correlation functional. *J. Chem. Phys.* **110**(11), 5029–5036 (1999)
14. Z.-S. Wu, W. Ren, L. Wen, L. Gao, J. Zhao, Z. Chen, G. Zhou, F. Li, H.-M. Cheng, Graphene Anchored with Co₃O₄ Nanoparticles as Anode of Lithium Ion Batteries with Enhanced Reversible Capacity and Cyclic Performance. *ACS Nano.* **4**(6), 3187–3194 (2010)
15. L. Zhang, T. Zhang, C. Wang, W. Jin, Y. Li, H. Wang, C. Ding, Z. Wang, First-principles insight into SnS₂/graphene heterostructure as potential anode materials for rechargeable lithium/sodium ion batteries. *Chem. Phys.* **594**, 112664 (2025)

16. L.B. Tang, P.Y. Li, T. Peng, H.X. Wei, Z. Wang, H.Y. Wang, C. Yan, J. Mao, K. Dai, X.W. Wu, Double-coated SnS with hierarchical carbon network as high-performance anode materials for sodium-ion batteries. *J. Electroanal. Chem.* **928**, 117077 (2023)
17. Z. Zhang, X. Shao, J. Fan, Z. Xiong, Y. Huo, L. Ran, H. Lu, W. Xiao, X. Lin, H. Liu, M. Xu, Tailored, Chem. Eng. J. **532**, 174340 (2026). V/Mn/Ti ratio unlocks high-performance phosphate cathodes for sodium-ion batteries
18. Q. Li, F. Yu, Y. Cui, J. Wang, Y. Zhao, J. Peng, Multilayer SnS-SnS₂@GO heterostructures nanosheet as anode material for Sodium ion battery with high capacity and stability. *J. Alloys Compd.* **937**, 168392 (2023)
19. K.A. Nguyen, D.A. Nguyen, A.K. An, A. Jang, Electrosorption based-removal of As(III) and Fluoride via interlayer-expanded Mn-doped La-Al-layered double hydroxides: Role of sodium dodecyl sulfate intercalation. *J. Environ. Chem. Eng.* **14**(3), 122168 (2026)
20. H. Peng, R. Ji, Z. Liu, Y. Bai, M. Wang, X. Huang, Enhanced Na⁺ adsorption by S-N Co-doped porous carbon from sodium gallate toward high-performance dual-carbon sodium-ion hybrid capacitors. *Chin. Chem. Lett.* **37**(5), 112417 (2026)
21. B. Ran, M. Li, J. Song, T. Zhao, W. Tang, B. Pang, H. Li, C. Yang, J. Zhang, C. Fu, Activating and Stabilizing Anionic Redox via High-Entropy Enhanced Mn-O Hybridization in Superlattice Cathodes for High-Energy Sodium-Ion Batteries. *Energy Storage Mater.* **86**, 104912 (2026)
22. Y. Bai, Y. Qin, P. Qiu, Boosting the acetone sensing of SnS nanoflakes by spin Mn substitution: a novel adsorption-desorption perspective. *Environ. Sci. : Nano.* **8**(4), 1096–1108 (2021)
23. J. Shi, Y. Wang, Q. Su, F. Cheng, X. Kong, J. Lin, T. Zhu, S. Liang, Pan, A. N-S co-doped C@SnS nanoflakes/graphene composite as advanced anode for sodium-ion batteries. *Chem. Eng. J.* **353**, 606–614 (2018)
24. B. Yan, L. Lin, H. Sun, T. Zhang, C. Xu, C. Sun, L. Zhang, X. Yang, Double-shelled NiS/SnS@N-doped carbon nanoboxes engineered from NiSn(OH)₆ cube templates for advanced sodium-ion battery anodes. *Chem. Eng. J.* **477**, 146950 (2023)
25. Y. Qin, S. Zhao, H. Wu, C. Sun, J. Xu, M. Yang, R. Shi, H. Bao, Synergistic modification mechanism of Mn-doped and N-doped carbon-coated FeS composites and their application in lithium-ion batteries. *J. Energy Storage.* **134**, 118300 (2025)
26. J. Xia, L. Liu, S. Jamil, J. Xie, H. Yan, Y. Yuan, Y. Zhang, S. Nie, J. Pan, X. Wang, G. Gao, Free-standing SnS/C nanofiber anodes for ultralong cycle-life lithium-ion batteries and sodium-ion batteries. *Energy Storage Mater.* **17**, 1–11 (2019)
27. J. Chen, P. Liu, K. Xu, Z. Hao, G. Tang, C. Zhu, Z. Ding, S. Yin, Z. Li, Z. Ding, Y. Wang, Z. Liu, S. Yu, X. Xin, F. Liu, Achieving long-term cycling stability in Na₃V₂(PO₄)₃ cathode material through polymorphic carbon network coating. *Carbon.* **238**, 120146 (2025)
28. B. Qu, C. Ma, G. Ji, C. Xu, J. Xu, Y.S. Meng, T. Wang, J.Y. Lee, Layered SnS₂-Reduced Graphene Oxide Composite -A High-Capacity, High-Rate, and Long-Cycle Life Sodium-Ion Battery Anode Material.

29. C. Ding, Z. Chen, C. Cao, Y. Liu, Y. Gao, Advances in Mn-Based Electrode Materials for Aqueous Sodium-Ion Batteries. *Nano-Micro Lett.* **15**(1), 192 (2023)
30. Y. Zheng, T. Zhou, C. Zhang, J. Mao, H. Liu, Z. Guo, Boosted Charge Transfer in SnS/SnO₂ Heterostructures: Toward High Rate Capability for Sodium-Ion Batteries. *Angew Chem. Int. Ed.* **55**(10), 3408–3413 (2016)
31. H.R. Jiang, Z. Lu, M.C. Wu, F. Ciucci, T.S. Zhao, Borophene, A promising anode material offering high specific capacity and high rate capability for lithium-ion batteries. *Nano Energy.* **23**, 97–104 (2016)
32. V. Augustyn, P. Simon, B. Dunn, Pseudocapacitive oxide materials for high-rate electrochemical energy storage. *Energy Environ. Sci.* **7**(5), 1597–1614 (2014)
33. T. Kang, D. Shen, S. Ni, Q. Chen, T. Li, X. Yang, J. Zhao, Pseudocapacitive charge storage induced by self-enhanced electrical conductivity and Li-ion diffusion in high performance Li₃VO₄@LiVO₂ anode for Li-ion batteries. *J. Alloys Compd.* **741**, 442–448 (2018)
34. C.J. Wen, R.A. Huggins, Thermodynamic and mass transport properties of LiIn. *Mater. Res. Bull.* **15**(9), 1225–1234 (1980)

Figures

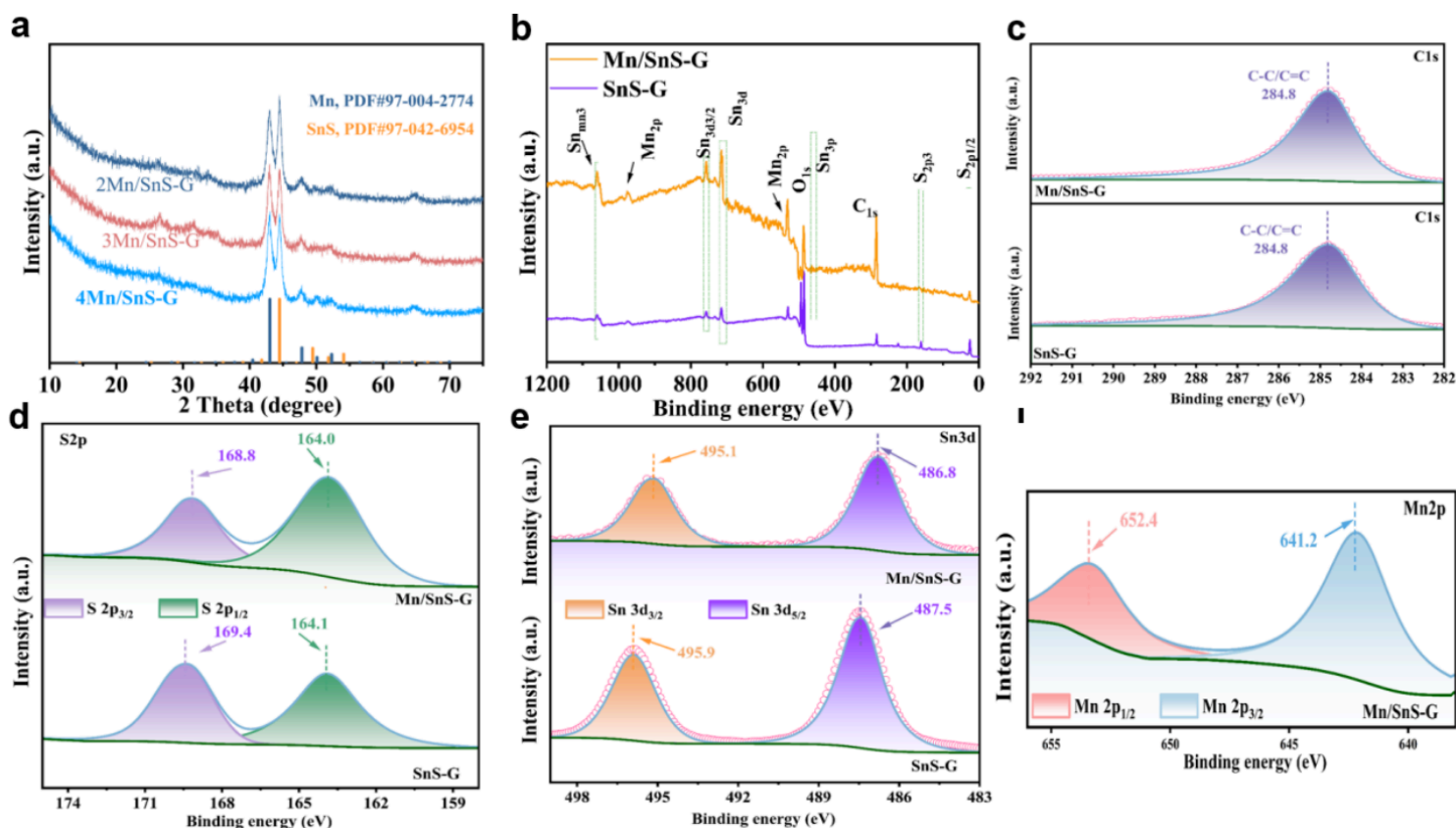


Figure 1

(a) Comparative XRD patterns of 2Mn/SnS-G, 3Mn/SnS-G, and 4Mn/SnS-G; (b) Survey XPS spectra of Mn/SnS-G and SnS-G; (c) C 1s XPS spectra of Mn/SnS-G and SnS-G; (d) S 2p XPS spectra of Mn/SnS-G and SnS-G; (e) Sn 3d XPS spectra of Mn/SnS-G and SnS-G; (f) Mn 2p XPS spectrum of Mn/SnS-G.

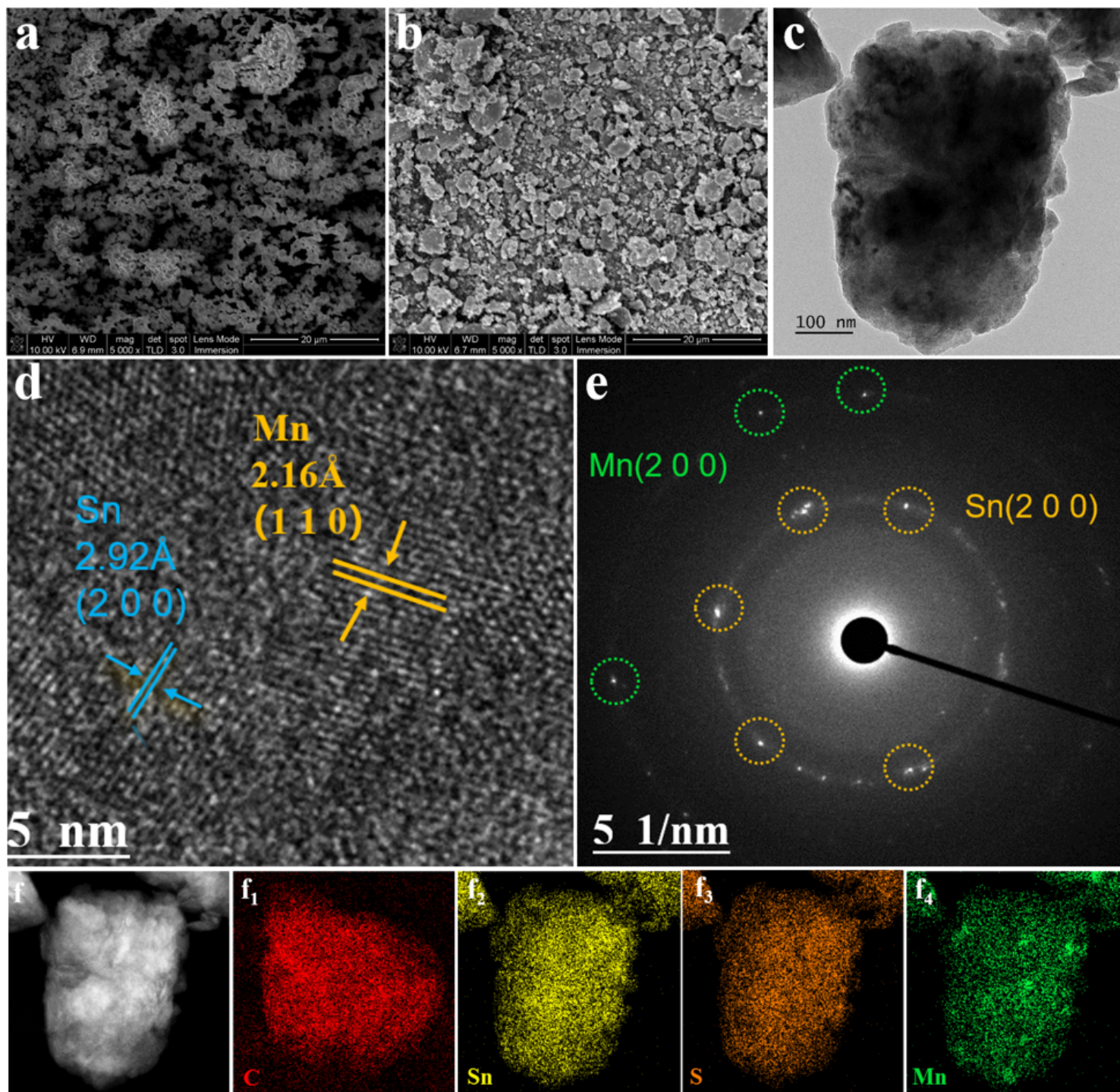


Figure 2

(a, b) SEM images of SnS-G and Mn/SnS-G; (c, d) TEM and HRTEM images of Mn/SnS-G; (e) SAED pattern of Mn/SnS-G; (f, f₁-f₄) Elemental mapping images of Mn/SnS-G showing the distribution of Mn, Sn, S, and C.

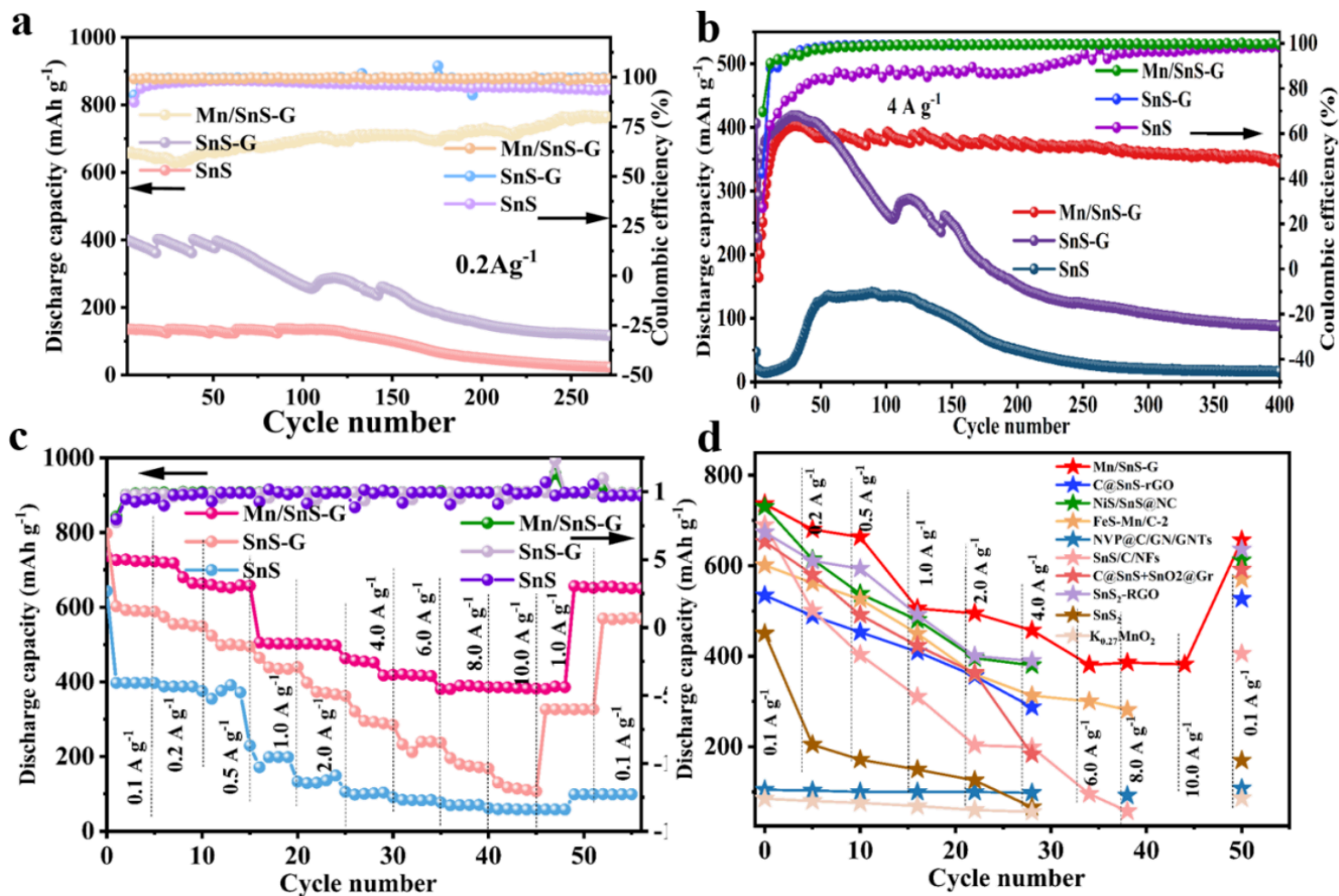


Figure 3

(a) Cycling stability of the Mn/SnS-G, SnS-G, and pristine SnS electrodes at a current density of 0.2 Ag⁻¹; (b) cycling stability of the Mn/SnS-G, SnS-G, and pristine SnS electrodes at a current density of 4 Ag⁻¹; (c) rate performance of the Mn/SnS-G, SnS-G, and pristine SnS electrodes; (d) rate performance comparison of Mn/SnS-G with C@SnS-RGO, NiS/SnS@NC, Mn-FeS/NC, NVP@C/GN/GNTs, SnS/C/NFs, C@SnS+SnO₂@Gr, SnS-RGO, SnS₂, and K_{0.27}MnO₂ [23-31].

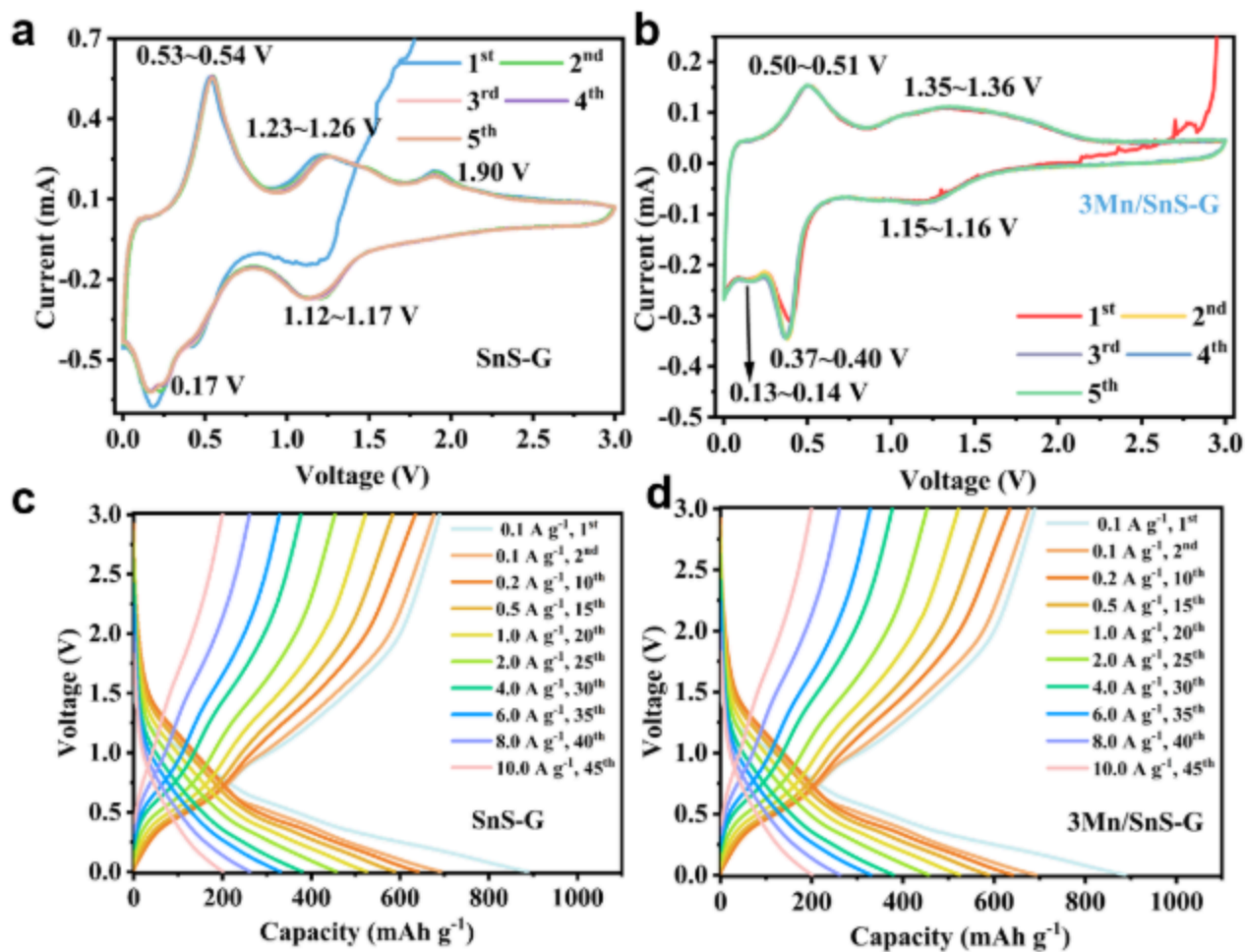


Figure 4

(a) CV curves of SnS-G; (b) CV curves of Mn/SnS-G; (c) discharge/charge curves of SnS-G extracted from rate-cycling test; (d) discharge/charge curves of Mn/SnS-G extracted from rate-cycling test.

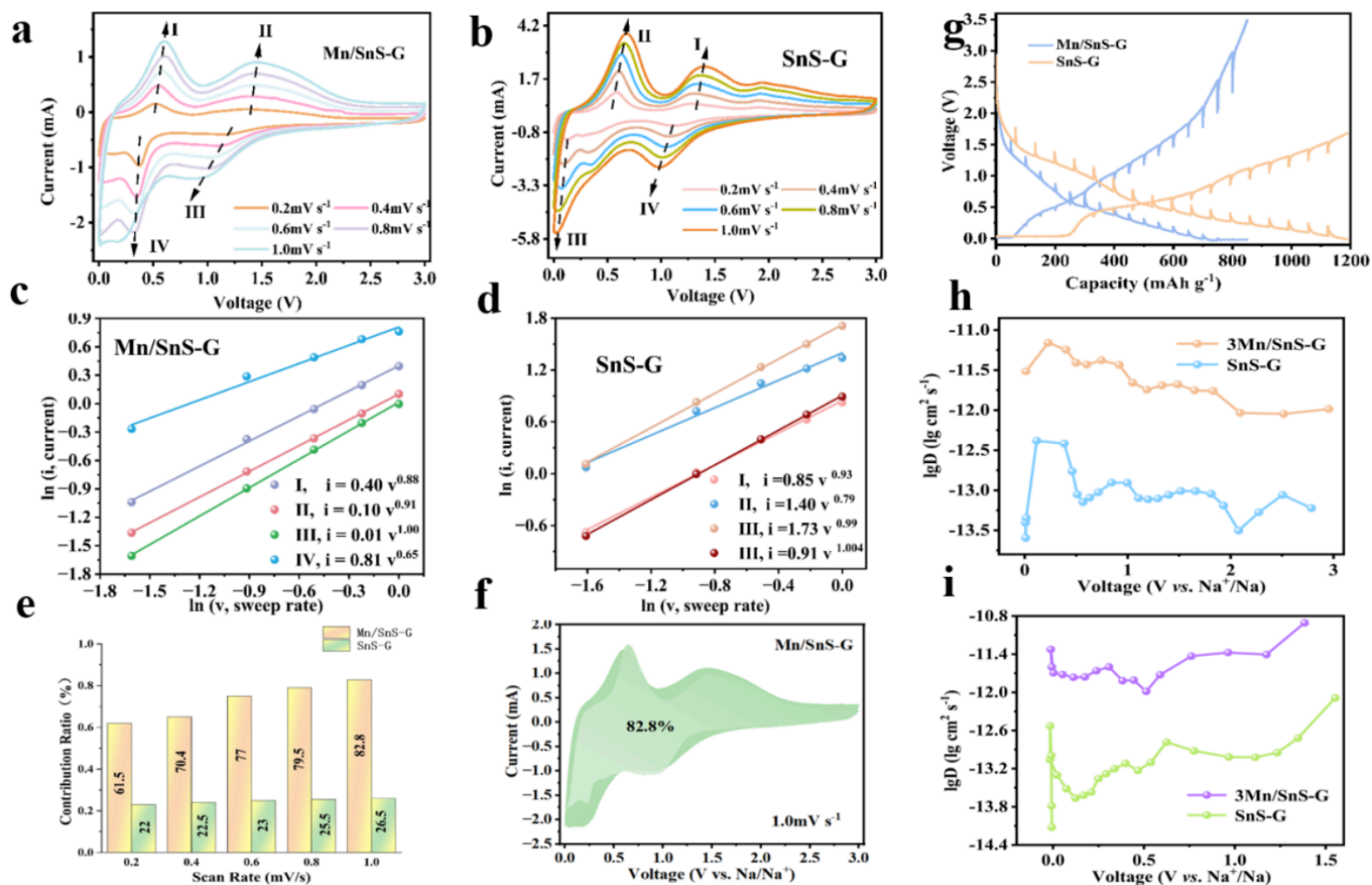


Figure 5

(a) CV curves of Mn/SnS-G measured at various scan rates; (b) CV curves of SnS-G measured at various scan rates; (c) b-values determined from the prominent peaks in the CV curves of Mn/SnS-G at different scan rates; (d) b-values determined from the CV curves of SnS-G at various scan rates; (e) surface pseudocapacitance of Mn/SnS-G at a scan rate of 1.0 mV s^{-1} ; (f) the calculated values obtained during the discharging process; (g) GITT curves of 3Mn/SnS-G and SnS-G; (h) the calculated values obtained during the charging process; (i) pseudocapacitance ratios of Mn/SnS-G and SnS-G at different scan rates.

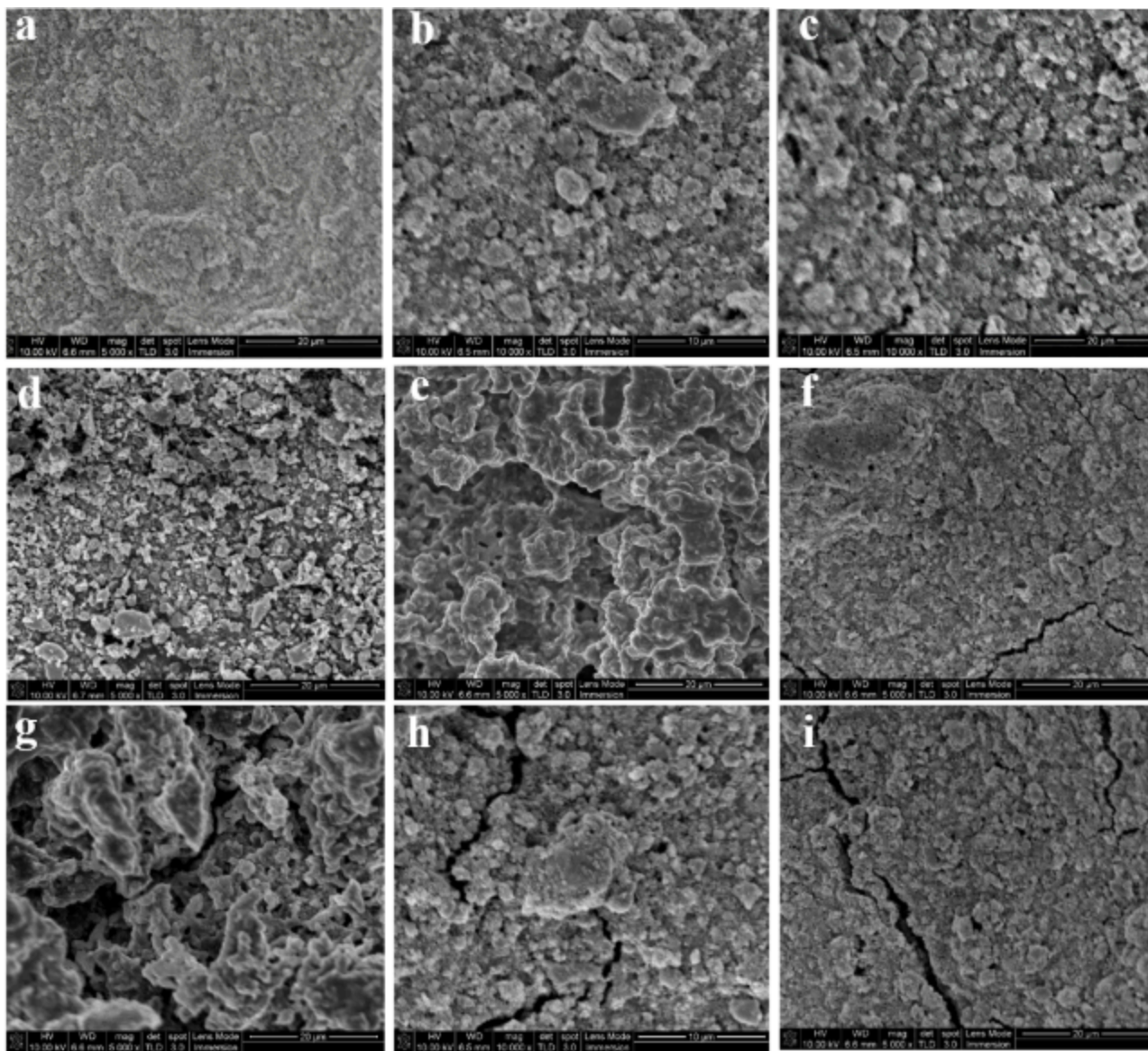


Figure 6

(a, b, c) SEM images of Mn/SnS-G in its pristine state, after 200 cycles, and after 400 cycles, respectively; (d, e, f) SEM images of SnS-G in its pristine state, after 200 cycles, and after 400 cycles, respectively; (g, h, i) SEM images of SnS in its pristine state, after 200 cycles, and after 400 cycles, respectively.

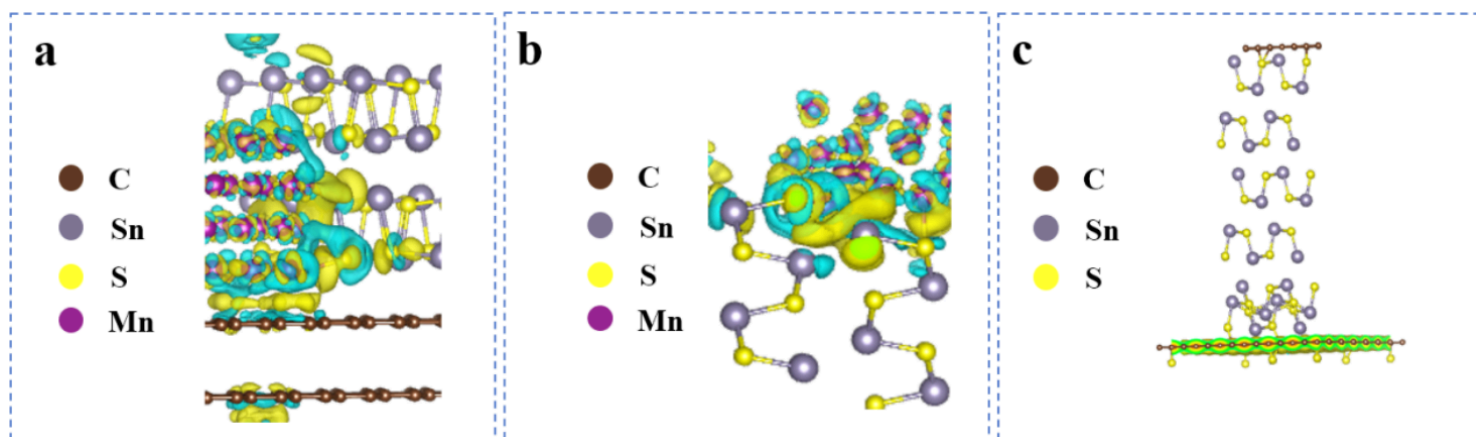


Figure 7

Charge density difference maps of (a) Mn/SnS-G, (b) Mn/SnS, and (c) SnS-G.

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