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Supporting information

Integrated Copper Host/Current Collector Engineering for Enhanced Sodium Storage in SeS₂ Electrodes

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Experimental section

Synthesis of Cu@CNT composite: Initially, 100 mg of carbon nanotubes (CNT) was ultrasonically dispersed into 40 mL of deionized water for 30 minutes. Subsequently, 600 mg of copper(II) acetate monohydrate $(Cu(CH_3COO)_2 \cdot H_2O)$ was dissolved in the above suspension, followed by further ultrasonication for 2 hours. The mixture was then transferred to an evaporating dish and heated at 100 °C for 12 hours to yield a black precursor powder. The final Cu@CNT composite was obtained by annealing this powder at 350 °C for 1 hour in ambient air, followed by a secondary annealing at 500 °C for 2 hours in a hydrogen-argon atmosphere (8% H₂, 92% Ar by volume).

Fabrication of CNT/SeS₂ and Cu@CNT/SeS₂: For CNT/SeS₂ synthesis, SeS₂ powder was uniformly mixed with CNT in a 1: 1mass ratio. The mixture was then vacuum-sealed in a glass tube and heated at 180 °C for 12 hours. The Cu@CNT/SeS₂ composite was prepared using an identical procedure, substituting Cu@CNT for CNT.

Material characterization: The crystalline structures of CNT/SeS₂ and Cu@CNT/SeS₂ were characterized using X-ray diffraction (XRD) on a Bruker D8 Advance diffractometer (40 kV, 40 mA) with Cu K α radiation. X-ray photoelectron spectroscopy (XPS) analyses were performed using Thermo Fisher EscalableXi+ equipment. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images were captured using a Hitachi SU8010 and a Thermo Fisher TALOS F200X (200 kV), respectively. Thermogravimetric analysis (TGA) was conducted using a TG209 F3 instrument from 40 °C to 700 °C at a heating rate of 10 °C min⁻¹ in air.

Electrochemical measurements: Electrodes were prepared by combining active materials (CNT/SeS₂ or Cu@CNT/SeS₂), carboxymethylcellulose sodium (CMC), and Ketjen Black in an 8: 1: 1 mass ratio, and stirring in distilled water for 30 minutes to form a slurry. This slurry was then coated onto copper (or aluminum) foil foil and dried in a vacuum oven at 60 °C for 12 hours. The electrodes were punched into 12 mm diameter discs. with an average SeS₂ loading of about 1.0 mg cm⁻². For high-loading experiments, electrodes with SeS₂ loading of 3.0 - 3.2 mg cm⁻² were also prepared. Electrochemical cells were assembled in an argon-filled glove box using CR2032 coin cell hardware, with 1 M NaPF₆ in dimethoxyethane (DME) as the electrolyte and Whatman GF/D glass fiber as the separator. Galvanostatic charge-discharge tests were conducted within a voltage window of 0.01 - 2.5 V using a Neware battery testing system. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements were carried out on an Ivium-n-Stat electrochemical workstation.



Fig. S1 XRD patterns of commercial SeS_2 and as-prepared CNT/SeS₂ powders.



Fig. S2 Morphological changes of SeS_2 powder. (a) SEM image of initial SeS_2 powder. (b) SEM image of SeS_2 powder applied to Cu current collector.

SEM analysis reveals that SeS_2 powder initially appears as large aggregates (Fig. S2a). A significant morphological transformation is observed upon coating onto Cu foil (Fig. S2b), indicating a potential chemical intereaction between SeS_2 and Cu.



Fig. S3 (a) XRD pattern and (b) SEM image of CNT/S coated on Cu foil. (c) XRD pattern and (d) SEM image of CNT/Se coated on Cu foil.

After applying CNT/S and CNT/Se slurries onto Cu foil and driing, the electrodes have been characterized by XRD and SEM. CNT/S shows CuS features (JCPDS No. 65-3588) in XRD (Fig. S3a) and clumped morphology in SEM (Fig. S3b). Conversely, CNT/Se exhibits distinct Se peaks (Fig. S3c) and lacks clumped morphology (Fig. S3d), indicating no reaction with Cu.



Fig. S4 TEM image of CNT/SeS_2 electrode after 70 cycles.



Fig. S5 Cross-sectional SEM image of pristine Cu foil, showing a thickness of 8 μ m.



Fig. S6 Analysis of battery failure due to Cu corrosion. (a) Charge-discharge profiles of high-loading electrode. (b) SEM image of CNT/SeS₂ electrode with high loading after 70 cycles.

Battery failure is observed at the 26^{th} cycle (Fig. S6a). The SEM image reveals a severe Cu corrosion reducing current collector thickness to 3.3 μ m (Fig. S6b), thereby leading to electrode detachment and battery failure.



Fig. S7 (a) XRD pattern, (b) SEM image and (c) TGA curve of Cu@CNT powder.

The XRD pattern in Fig. S7a showcases several sharp peaks corresponding to Cu (JCPDS No. 00-004-0836), confirming the crystalline nature of Cu particles in the composite. The SEM image in Fig. S7b reveals finely dispersed Cu nanoparticles securely anchored onto the surfaces of CNTs, highlighting the successful synthesis of the Cu@CNT composite with a uniform distribution of Cu particles. The TGA depicted in Fig. S7c is segmented into two distinct thermal events. The initial increase in mass observed below 400°C is attributed to the oxidation of Cu to copper oxide (CuO) due to its reaction with atmospheric oxygen. This is followed by a significant weight loss beyond 400°C, which is associated with the combustion of carbon content within the composite. Quantitative analysis of the TGA data allows for the determination of the carbon content within the Cu@CNT powder, estimating it to be approximately 43.7%.



Fig. S8 Cross-sectional SEM image of pristine Cu@CNT/SeS₂ electrode.

The SEM image shows that the thickness of pristine Cu@CNT/SeS₂ electrode is 7.9 μ m, suggesting a minimal corrosion (compared to 8.0 μ m).



Fig. S9 SEM images of Cu@CNT/SeS₂ electrode with SeS₂ loading of about 1.0 mg cm⁻²: (a) pristine Cu@CNT/SeS₂ electrode; (b) Cu@CNT/SeS₂ electrode after 70 cycles.



Fig. S10 SEM images of Cu@CNT/SeS₂ electrode with high loading (3 mg cm⁻²): (a) pristine Cu@CNT/SeS₂ electrode; (b) Cu@CNT/SeS₂ electrode after 70 cycles.

Thickness measurements show little change pre- and post-cycling, from 7.9 μ m to 7.8 μ m, indicating stability under high loading. (Fig. S10b).



Fig. S11. Nyquist plots of Cu@CNT/SeS₂ on different current collectors: (a) Cu; (b) Al.



Fig. S12. Cycling performance of CNT/SeS₂ composite electrodes at varied CNT/SeS₂ mass ratios. Panel (a) illustrates the specific capacities derived from the active SeS₂ mass in the composites, showcasing how the balance between CNTs and SeS₂ affects the material's utilization and electrochemical efficiency. Panel (b) details the specific capacities relative to the total mass of the electrodes, highlighting the impact of varying CNT/SeS₂ ratios on the overall electrode performance and mass efficiency.

This comparison elucidates the optimal CNT/SeS₂ mass ratio for enhancing the electrochemical characteristics of the electrodes by achieving a synergistic balance between conductivity improvement and mass contribution. As illustrated in **Fig. S12**, reveal that a balanced CNT/SeS₂ ratio is crucial for maximizing electrode performance. Specifically, at a mass ratio of 3:7 (CNT/SeS₂), the limited addition of CNTs resulted in suboptimal conductivity and low SeS₂ utilization, yielding a specific capacity of approximately 305 mAh g⁻¹. Conversely, increasing the CNT content to a 7:3 mass ratio significantly enhanced the specific capacity of SeS₂ to 810 mAh g⁻¹. However, this high CNT content led to an increased electrode mass, adversely affecting the overall specific capacity of the electrode. Given these observations, we determined that a 1:1 CNT/SeS₂ mass ratio represents an optimal balance, effectively maximizing the utilization rate of SeS₂ while maintaining an appropriate electrode mass, as detailed in **Fig. S12**. This ratio was thus chosen for further research and development within our study.



Fig. S13. Electrochemical sodium storage performance of CNT at 0.2 A g⁻¹: (a) cycling performance; (b) charge-discharge profiles at different cycles.

CNTs exhibit a significant specific capacity of approximately 95 mAh g^{-1} at a current density of 0.2 A g^{-1} . This finding underscores the active participation of CNTs in sodium storage, contributing to the overall capacity of the electrode. The insights gained from this analysis are crucial for understanding the multifaceted contributions of composite materials in sodium-ion batteries and are instrumental in guiding the optimization of electrode compositions for enhanced electrochemical performance.



Fig. S14. Auger electron spectrum of Cu@CNT/SeS₂ powder.

Upon detailed examination of the XRD pattern, it was observed that significant Cu peaks were indeed not present, suggesting that the Cu might have fully reacted to form $Cu_{1.95}S$. This hypothesis was further supported by Auger electron spectroscopy analysis, which revealed a distinct peak of Cu⁺ at 917.5 eV, indicating the conversion of metallic Cu to Cu⁺ in the composite. This analysis is crucial for confirming the complete reaction of Cu within the composite.



Fig. S15. Investigation of corrosion on Cu foil using Cu@CNT powder with different Cu concentrations. (a) TGA curve for Cu@CNT containing 49.7% Cu. (b-c) SEM images of the corresponding Cu@CNT/SeS₂ electrode before and after 70 cycles. (d) TGA curve for Cu@CNT with a higher concentration of 60.7% Cu. (e-f) SEM images of the corresponding Cu@CNT/SeS₂ electrode before and after 70 cycles.

We conducted a series of experiments to evaluate the impact of varying Cu content within the Cu@CNT/SeS₂ composite on the corrosion behavior of Cu foil during electrochemical cycling. By adjusting the Cu content in the composite, we observed a nuanced relationship between Cu concentration and corrosion rate. Specifically, a lower Cu content was associated with a higher rate of corrosion, while an increased Cu content effectively mitigated this effect, albeit with potential repercussions on the electrode's specific capacity. For instance, a composite with 60.7% Cu mass resulted in a limited corrosion rate of 1.25% after 70 cycles. Conversely, decreasing the Cu mass to 49.7% led to an elevated corrosion rate of 10.0%, showcasing a direct correlation between Cu content and corrosion resistance. Our study underscores the critical balance required between optimizing Cu content to minimize corrosion while ensuring the electrochemical performance of the electrode is not compromised.



Fig. S16. Cycling performance of the Cu@CNT/SeS₂ electrode at elevated current density. This figure illustrates the electrode's cycling stability when subjected to a higher operational current density of 3 A g^{-1} , following initial activation cycles conducted at lower current densities of 1 A g^{-1} and 2 A g^{-1} .

Prior to this assessment, we activated the battery through a preconditioning process, involving 10 cycles each at current densities of 1 A g⁻¹ and 2 A g⁻¹, respectively, to ensure stable electrochemical behavior. The extended testing at 3 A g⁻¹ revealed that the battery maintains stable performance across the cycles, characterized by consistent capacity retention and high coulombic efficiency. This stability is attributed primarily to the formation of $Cu_{1.95}S$ and $Cu_{1.8}Se$ phases, which exhibit excellent electrical conductivity and contribute to the effective suppression of the shuttle effect. The presence of these compounds likely plays a crucial role in enhancing the electrode's ability to handle higher current densities without significant degradation.