

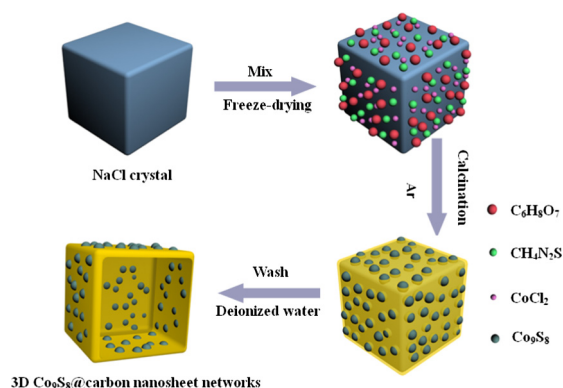


## Regular Article

## Cobalt sulfide nanoparticles anchored in three-dimensional carbon nanosheet networks for lithium and sodium ion batteries with enhanced electrochemical performance

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## GRAPHICAL ABSTRACT

3D Co<sub>9</sub>S<sub>8</sub>@CnNs composite is successfully fabricated by a simple route and delivers outstanding electrochemical performance for LIBs/SIBs.

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## ABSTRACT

In order to improve the conductivity and electrochemical activity, Co<sub>9</sub>S<sub>8</sub> nanoparticles anchored in three-dimensional carbon nanosheet networks (3D Co<sub>9</sub>S<sub>8</sub>@CnNs) are fabricated by a simple strategy with the assistance of NaCl. Combining the advantages of nanoscale and porous structure, 3D Co<sub>9</sub>S<sub>8</sub>@CnNs can retard the aggregation of Co<sub>9</sub>S<sub>8</sub> nanoparticles, provide abundant electrochemical active sites, as well as accommodate the mechanical stress during the cycling of lithium ion batteries (LIBs) or sodium ion batteries (SIBs). Thus, when evaluated as an anode for LIBs, the as-prepared 3D Co<sub>9</sub>S<sub>8</sub>@CnNs electrode exhibits outstanding electrochemical performance with a high reversible capacity of 935 mAh g<sup>-1</sup> after 200 cycles at 0.25 A g<sup>-1</sup>. As for SIBs, it also delivers superior cycling stability with a capacity of 249 mAh g<sup>-1</sup> after 50 cycles at 0.1 A g<sup>-1</sup>. These results demonstrate that 3D Co<sub>9</sub>S<sub>8</sub>@CnNs composite has potential to be utilized as an anode material for LIBs/SIBs with enhanced electrochemical performance.

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## 1. Introduction

Owing to the fast charge-discharge rates, reliable stabilities, and long cycle lives, rechargeable lithium-ion batteries (LIBs) have long been the predominant power source for portable devices, electronic vehicles and power grids [1–3]. With the social progress and quick development of electronic products, considerable efforts have been made for the demand of high-performance electrode materials [4–7]. On this basis, a wide variety of transitional metal sulfides have been widely investigated based on their higher theoretical specific capacities, larger than that of the commercial carbonaceous anodes ( $372 \text{ mAh g}^{-1}$  for graphite) [8,9]. Among them, cobalt sulfide ( $\text{Co}_9\text{S}_8$ ), with low-cost, high theoretical storage capacity ( $539 \text{ mAh g}^{-1}$ ) as well as widespread availability, has been regarded as an ideal substitute for commercial carbonous anodes for the next-generation LIBs. However, like the other metal sulfides,  $\text{Co}_9\text{S}_8$  also exhibits significant capacity fading induced by large volume variation and limited conductivity for impacting the electron or ion transport during lithium insertion and extraction processes [10].

To accommodate these issues for higher capacity retention, substantial measures have been reported. One strategy is designing  $\text{Co}_9\text{S}_8$  with special morphologies such as hollow spheres [11], rose-like [12] or nanosheets [13], which can be beneficial to the diffusion of lithium ion and efficiently buffer the mechanical strain. While, the undesirable side reactions and the formation of thick solid electrolyte interphase (SEI) films occur frequently on their surfaces. And this could be induced by the high surface-to-volume ratio and large surface free energy of the microstructure, thereby leading to the capacity fading and safety problems [14]. Another effective strategy is modifying  $\text{Co}_9\text{S}_8$  with conductive carbonous materials. In this context, a number of  $\text{Co}_9\text{S}_8$ /carbon composites have been exploited as anode materials for LIBs, such as graphene/ $\text{Co}_9\text{S}_8$  nanocomposite paper [15],  $\text{Co}_9\text{S}_8$  nanoflakes on graphene [16], multiwalled carbon nanotube@ $\text{a-C@Co}_9\text{S}_8$  composites [17] and graphene/ $\text{Co}_9\text{S}_8$  nanoparticles [18]. For the synthesis of the above  $\text{Co}_9\text{S}_8$ /carbon composites, hydrothermal or solvothermal methods have been considered as the typical approaches. While, these methods usually need complicated synthesis processes which are tedious, costly and time-consuming. In addition, the synthesized  $\text{Co}_9\text{S}_8$ /carbon composites usually exhibit limited capacities and poor cycling stabilities. These serious issues would greatly hinder the large-scale application of  $\text{Co}_9\text{S}_8$  for LIBs. Thus, it is highly necessary to find a new approach to produce  $\text{Co}_9\text{S}_8$ /carbon composite with unique structure, which cannot only provide more electrochemical active sites, but also accommodate the mechanical stress during charge/discharge processes.

Lately, sodium ion batteries (SIBs) have attracted considerable interests as a promising alternative to LIBs based on these advantages such as the cheap sodium resource, wide distribution and earth-abundant [19,20]. Unfortunately, SIBs usually exhibit low specific capacities, short lifetimes and poor rate capabilities on account of the larger radius of sodium ions ( $1.02 \text{ \AA}$ ) than that of lithium ions ( $0.59 \text{ \AA}$ ) [21]. Thus, unremitting efforts have been devoted to exploring novel anode materials for SIBs with superior electrochemical performance. Due to their appropriate reaction potential for sodium storage, metal sulfides with high theoretical specific capacities have been regarded as promising anode materials for rechargeable SIBs [22,23]. Up to now, only a few cobalt sulfides have been investigated in accordance with their sodium storage capability. Among them,  $\text{Co}_9\text{S}_8$  also has attracted increasing attention for SIBs because of its high capacity, low toxicity and high availability. Furthermore, to the best of our knowledge, the study of structure designed  $\text{Co}_9\text{S}_8$ /carbon composites and their enhanced Na-storage performance have been scarcely reported.

Herein,  $\text{Co}_9\text{S}_8$  nanoparticles homogeneously anchored in three-dimensional carbon nanosheet networks (3D  $\text{Co}_9\text{S}_8$ @CNNs) were successfully synthesized by a simple method. With the aid of NaCl as a template, the carbon nanosheet created a 3D architecture which can further improve the conductivity and electrochemical activity. Meanwhile, the SEM and TEM results also indicated that  $\text{Co}_9\text{S}_8$  nanoparticles can be uniformly anchored onto and embedded in the carbon nanosheets by this method. Based on their unique structure, the as-synthesized 3D  $\text{Co}_9\text{S}_8$ @CNNs composite delivered high reversible capacity, good cycling stability together with excellent rate capability and could be acted as a potential anode material for LIBs/SIBs with high performance.

## 2. Experimental

### 2.1. Synthesis of 3D $\text{Co}_9\text{S}_8$ @CNNs composite

The 3D  $\text{Co}_9\text{S}_8$ @CNNs composite was fabricated via a simple approach. Firstly,  $0.214 \text{ g}$  of cobalt dichloride ( $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ ),  $0.137 \text{ g}$  of thiourea ( $\text{CH}_4\text{N}_2\text{S}$ ),  $0.265 \text{ g}$  of citric acid ( $\text{C}_6\text{H}_8\text{O}_7$ ) and  $3.600 \text{ g}$  of NaCl were dissolved in  $20 \text{ ml}$  of deionized (DI) water by magnetic stirring. Then, the dry gel was obtained after freeze-drying. Subsequently, the dry gel was ground into fine composite powder, placed into a quartz boat and heated at  $700 \text{ }^\circ\text{C}$  for  $3 \text{ h}$  in a tube furnace under Ar. After cooling naturally, the NaCl template was removed by DI water to obtain the final 3D  $\text{Co}_9\text{S}_8$ @CNNs composite. For comparison, the  $\text{Co}_9\text{S}_8/\text{C}$  composite was prepared via the similar process described above except adding NaCl template. The pure  $\text{Co}_9\text{S}_8$  and CNNs were obtained by the similar process in the absence of  $\text{C}_6\text{H}_8\text{O}_7$  and  $\text{CoCl}_2 \cdot \text{CH}_4\text{N}_2\text{S}$ , respectively.

### 2.2. Materials characterization

X-ray powder diffraction (XRD) patterns of the samples were achieved by a diffractometer (Rigaku) with  $\text{Cu K}\alpha$  radiation ( $\lambda = 0.15418 \text{ nm}$ ) at a scanning rate of  $0.03^\circ \text{ s}^{-1}$  with a  $2\theta$  range from  $10$  to  $80^\circ$ . The morphology and microstructure investigations were detected by field scanning electron microscopy (SEM, JEOL JSM-6390A) and high-resolution transmission electron microscopy (TEM,  $\text{G}^2 \text{ F20 S-TWIN}$ ). X-ray photoelectron spectroscopy (XPS) was conducted on a PHI-5400 electron spectrometer with  $\text{Mg K}\alpha$  X-ray as the excitation source. Raman spectrum was recorded using a Nicolet Almega dispersive Raman spectrometer with an excitation laser wavelength of  $532 \text{ nm}$ . The specific surface areas and pore size distribution of the products were calculated by nitrogen adsorption through the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods. Thermogravimetric analysis (TGA, SDT Q600) was performed in air atmosphere from room temperature to  $600 \text{ }^\circ\text{C}$  at a heating rate of  $10 \text{ }^\circ\text{C min}^{-1}$ .

### 2.3. Electrochemical measurements

Electrochemical measurements of the prepared materials were investigated using 2025 coin-type half cells fabricated in an argon-filled glove box. The working electrodes were prepared by mixing the active materials, acetylene black and polyvinylidene fluoride in a mass ratio of  $80:10:10$  in *N*-methyl-2-pyrrolidinone and pasted onto a Ni foam ( $14 \text{ mm}$  in diameter) followed by vacuum-dried at  $80 \text{ }^\circ\text{C}$  for  $12 \text{ h}$ . The loading density of each electrode was about  $2.0 \text{ mg cm}^{-2}$ . For the lithium cell, metallic lithium foil was used as the counter electrode. The electrolyte consisted of a mixture of  $\text{LiPF}_6$  ( $1 \text{ M}$ ) in diethyl carbonate (DEC), dimethyl carbonate (DMC) and ethylene carbonate (EC) at a  $1:1:1$  volume ratio. For the sodium cell, metal sodium was used as counter electrode. The electrolyte was  $\text{NaClO}_4$  ( $1 \text{ M}$ ) in a mixture of propylene car-

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