# Conductive bridging effect of TiN nanoparticles on the electrochemical performance of TiN@CNT-S composite cathode

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## ARTICLE INFO

## ABSTRACT

Improving the reaction kinetics of cathode and preventing the dissolution of polysulfides are two of the key strategies of developing the high-performance lithium-sulfur (Li-S) batteries. Herein, we propose a multi-porous conductive architecture through bridging conductive TiN nanoparticle over the surface of CNT-S composite. The as-prepared TiN@CNT-S composite cathode delivers the superior initial specific capacity of $1269\,mAh\,g^{-1}$ at 0.05C and as high as $586\,mAh\,g^{-1}$ at 2C. The reversible capacity of the TiN@CNT-S composite cathode is about two times higher than the bare cathode without TiN conductive bridging at 1C over 400 cycles. A high areal capacity of $4.0\,mAh\,cm^{-2}$ was realized for the TiN@CNT-S composite cathode with a high areal sulfur loading of $5.4\,mg\,cm^{-2}$ at a current rate of 0.5C over 50 cycles. The enhancements in the electrochemical performances are mainly ascribed to the TiN bridged highly conductive structure; the formation of the strong chemical interaction of S-N-Ti bond for polysulfides trapping provided by the chemically polar TiN, which is verified by the ultraviolet visible (UV) spectra and X-ray photoelectron spectroscopy (XPS) analyses.

## 1. Introduction

With the rapid development of electric vehicles, portable electronics and grid energy storage, the traditional Li-ion batteries are insufficient to satisfy the ever-increasing demand of high energy density storage due to their limited cathode capacity ($\sim280\,mAh\,g^{-1}$) [1]. Lithium-sulfur (Li-S) battery has been considered as one of the most promising candidates for the next generation rechargeable batteries owing to its high theoretical capacity of $1675\,mAh\,g^{-1}$ and overwhelming theoretical specific energy of $2500\,Wh\,kg^{-1}$ [2–4]. Although the highly competitive advantages of Li-S battery, its practical utilization is seriously impeded due to the following issues: the elemental sulfur and discharged product (lithium sulfides) have poor electronic and ion conductivity; the large volume expansion of $\sim80\%$ from S to $Li_2S$ may lead to dramatic structure failure of the cathode; the highly soluble intermediate polysulfides ($Li_2S_n$, $4 \leq n \leq 8$) could easily migrate to lithium anode inducing the so-called shuttle effect during the redox process. These issues can directly bring about the poor cycling stability, inferior rate ability and short service life of the Li-S battery [5–7].

Many kinds of the carbonaceous host of sulfur have been tried to mitigate the above problems of Li-S battery, such as the mesoporous carbon, carbon sphere, carbon nanofiber, carbon nanotubes (CNTs), carbon paper, graphene and 3D graphene [8–14]. Some literatures also reported smart architectures or advanced techniques for the functionization of carbonaceous host [15–19]. Among those carbonaceous materials, the CNTs has been widely used as the conductive framework in the cathodes of Li-S battery [16,17,20,21], which exhibits a more effective electronically conductive network than the traditional carbon black, resulting in a significant improvement in the specific capacity [22–24]. However, the cycling stability of the cathode based on CNTs host is rather poor and the shuttle effect is rather serious because of the weak interaction between non-polar CNTs and polar polysulfides [25]. What's more, the effective electron transfer can only take place along the CNTs axis, which is hard to happen along the transverse directions from one CNT to another CNT. Furthermore, trapping the polysulfides from the cathode is another requisite factor to realize the long cycling performance of Li-S battery. Thus, it is worthwhile to find a route to strengthen the trapping ability of

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CNTs and the conductivity along the transverse direction from one CNT to nearby CNT for a high-performance Li-S battery.

Regarding the polysulfide trapping, the heteroatoms (O, S, N and B) are successfully doped to enhance the chemical interactions of the carbon matrix with the polysulfides [26–28]. Besides, various metal oxides (MOs), including $TiO_2$, $MnO_2$, $MoO_2$ and $La_2O_3$ as functional absorbent are also highly effective in trapping polysulfides owing to their polar characteristic [29–33]. However, most of the MOs are less conductive than the carbon materials and finally impede the electron transport pathways, and not helpful for developing the capacity of Li-S battery. Recently, Titanium nitride (TiN) has attracted researchers' interest greatly owing to its excellent conductivity and chemical stability. It was reported that the good conductive TiN nanoparticles have strong ability of trapping polysulfides [34–37] originated from not only the strong bonding between S and N atoms but also the polar characteristic. Reasonably, these features of TiN nanoparticles could mitigate the demerits of CNTs as the host of sulfur. Thus, it is scientifically interesting and practically useful to investigate the effect of TiN nanoparticles on the electrochemical behavior of CNT-S composite cathode.

In this work, we combined the conductive CNTs network with the polysulfide absorptive reagent TiN nanoparticles to form a multi-porous conductive structure of TiN@CNT-S composite as cathodes of Li-S battery. The TiN nanoparticles not only act as the bridges to strengthen the transverse conductivity from one sulfur wrapped CNT to another CNT, but also work as the strong trapping sites of polysulfides by physical and chemical absorption. As a result, the electrochemical performance of TiN@CNT-S cathode is significantly improved by combining with the conductive TiN nanoparticles.

## 2. Experimental

### 2.1. Preparation of CNT-S composite

The commercial CNTs (Cnano, China, Fltube 9000, 10 μm × 10 nm) were purified by strong acid mixture ($HNO_3$:$H_2SO_4$ = 1:3). The CNTs were put into the acid mixture and stirred constantly at 70 °C for 2 h, and then diluted with deionized water. After that, the dilution was vacuum filtrated and washed by deionized water repeatedly, and dried for 24 h. The $Na_2S_x$ solution was prepared following the processes as reported in the literature [14]: $Na_2S\bullet9H_2O$ (1.821 g) and the sublimed sulfur of 0.72 g (Aladdin, >99.95%) were put into 25 mL deionized water, and stirred at room temperature to form homogenous solution. Purified CNTs were dispersed into deionized water by means of sonication for 4 h. Then, $Na_2S_x$ solution was proportionally dripped into the dispersion slowly with strong magnetic stirring. 2 mol L$^{-1}$ HCOOH solution was added dropwise to the dispersion of CNTs with $Na_2S_x$ to in-situ deposit elemental S with continuous stirring. Through stirring overnight, the as-deposited mixture was filtrated and washed by deionized water for many times to remove soluble impurities. The filtrated product was dried at 60 °C for 24 h; finally, the product was sealed in a reactor full of argon gas and heated at 155 °C for 12 h to obtain CNT-S composite.

### 2.2. Preparation of TiN@CNT-S composites

Through sonication, TiN nanoparticles (Aladdin, 99.9%, diameter ∼ 20 nm) with a certain proportion were dispersed into 50 mL deionized water, and the prepared CNT-S composite of 0.24 g was dispersed into 600 mL deionized water. The two solutions were mixed together and continuously stirred overnight. The mixed solutions were filtrated and washed by the deionized water, and then was dried at 60 °C for 24 h to realize the bridging effect of TiN nanoparticles among the sulfur loaded CNT. (Without particular specification in this work, the TiN content in the TiN@CNT-S composite is 10 wt%). The TiN@CNT composite was prepared by the same method without sulfur loading.

### 2.3. Analysis of polysulfide adsorption

0.092 g $Li_2S$ (Sigma, 99.98%) and 0.448 g sulfur were dissolved into 10 mL mixed solvent (DOL/DME, 1:1 in volume, Suzhou China) to form 0.2 mol L$^{-1}$ homogeneous $Li_2S_8$ solution through stirring. Then, 0.2 mol L$^{-1}$ $Li_2S_8$ solution was diluted to 0.005 mol L$^{-1}$ by DOL/DME solvent. The diluted $Li_2S_8$ solution was filled into three screw-cap vials (8 mL per vial). The CNTs and TiN@CNT absorbents with the same mass of 0.05 g were soaked into the two of the vials for 8 h. Then the coloration of the solutions was recorded by a digital camera and the absorbance was evaluated by ultraviolet visible (UV-vis) spectra. All the operation processes were performed in a glove box full of the high pure Ar gas.

### 2.4. Materials characterization

The X-ray diffraction was collected on a XRD-7000S X-ray diffractometer (Cu-$K\alpha$, λ = 0.15418 nm) in a 2θ range from 10° to 80°. The morphology of the composites was observed with a Germany MERLIN Compact Scanning Electron Microscope (SEM) and a Tecnai G2 F20 S-TWIN Transmission Electron Microscope (TEM)
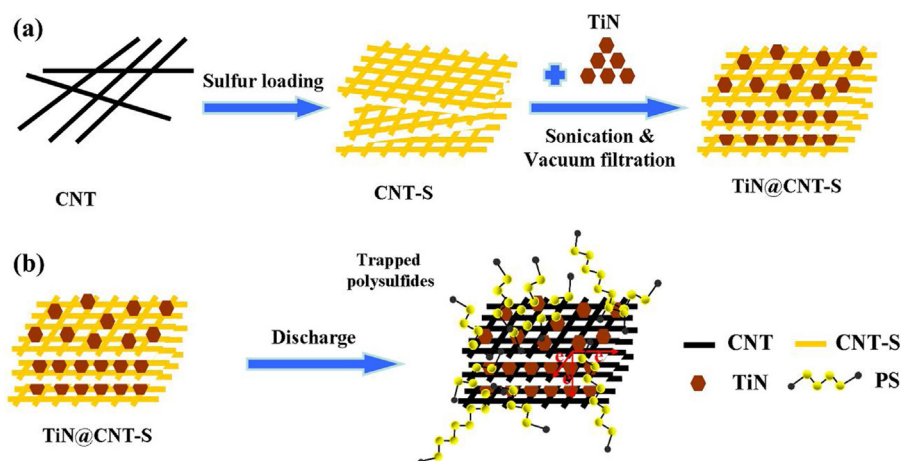


**Fig. 1.** Schematic illustration of (a) fabrication process and (b) the trapping mechanism of polysulfides and electron transfer pathway of TiN@CNT-S composite.