



# Mesoporous, conductive molybdenum nitride as efficient sulfur hosts for high-performance lithium-sulfur batteries



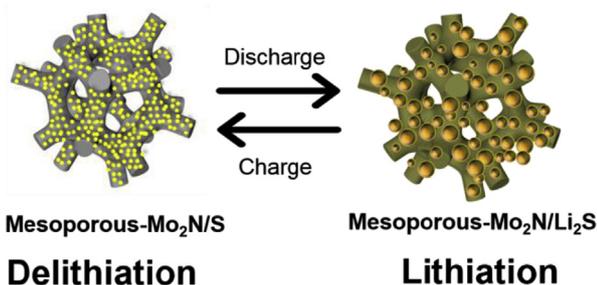
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## HIGHLIGHTS

- Mesoporous, conductive Mo<sub>2</sub>N is synthesized via template-assisted approach.
- Excellent conductivity of Mo<sub>2</sub>N improves the sulfur utilization.
- Mesostructure in Mo<sub>2</sub>N increases polar interface for chemisorption with polysulfides.
- Mesoporous Mo<sub>2</sub>N enhances physical confinement with polysulfides.

## GRAPHICAL ABSTRACT



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## ABSTRACT

The insulating nature of sulfur and the shuttling of polysulfides are two major fundamental issues that have to be tackled in Lithium-sulfur (Li-S) batteries, generally leading to low sulfur utilization and fast capacity decay. Constructing sulfur hosts with both excellent conductivity and efficient polysulfides immobilization is critical to the successful implementation of Li-S batteries. Herein, mesoporous molybdenum nitride (Mo<sub>2</sub>N) with interconnected structures is readily designed as sulfur hosts to resolve the low conductivity and polysulfides dissolution issues. The specific surface area and the conductivity of the mesoporous Mo<sub>2</sub>N are verified to be 121 m<sup>2</sup> g<sup>-1</sup> and 1 × 10<sup>5</sup> S m<sup>-1</sup>, respectively. Along with its high polarity enabling the chemisorption of polysulfides, the as-obtained mesoporous Mo<sub>2</sub>N is promising as sulfur host. The polysulfides dissolution is efficiently suppressed owing to the fruitful nanopores in the mesoporous Mo<sub>2</sub>N that offer more exposed polar interfaces for intensive chemical affinity/adsorption with polysulfides. Encouragingly, the as-prepared mesoporous, conductive and polar Mo<sub>2</sub>N with sulfur delivers superior capacity of 995 mA h g<sup>-1</sup>, long cycle stability (91.9% capacity retention after 100 cycles), superior to those of Nonporous-Mo<sub>2</sub>N/S and Mesoporous-MoO<sub>3</sub>/S. Our results reveal that vivid engineering of metal nitrides via creating nanopores is promising for pursuing high-performance Li-S batteries.

## 1. Introduction

The ever-increasing demand for energy storage systems with high energy density holds the key to the success of future energy-sustainable

and energy-efficient economy. Lithium-sulfur (Li-S) batteries have been gaining soaring attentions owing to the high theoretical specific capacity (1675 mA h g<sup>-1</sup>) of elemental sulfur as well as its environmental benignity and natural abundance [1–6]. Unfortunately, Li-S batteries

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still suffer from several challenges such as low sulfur utilization and rapid capacity decay. These drawbacks mainly arise from the insulating nature of sulfur and its discharge products and the shuttle effect caused by dissolution of intermediate lithium polysulfides (LiPSs) into the electrolyte [7–11]. Hence, constructing sulfur hosts with both excellent conductivity and efficient entrapment of soluble LiPSs has been regarded as the first step to demonstrate the potential of Li-S batteries.

Tremendous attempts have been devoted to addressing the above challenging issues in the past several years. Benefiting from sufficient conductivity and tailorable porosity, porous carbons were the most widely used materials at the early stage, such as microporous carbons [12,13], mesoporous carbons [14,15], hierarchical porous carbons [16,17], carbon nanotubes/fibers [18–20], carbon spheres [21–23], graphene [24–27], or their hybrids [28–30]. By virtue of the conducting networks and enhanced physical entrapment of the LiPSs, a pronounced capacity enhancement was achieved during the initial cycles. However, a long cycling capacity fading was not well resolved probably because intrinsically nonpolar carbon is less efficient in immobilizing polar LiPSs. Although the affinity of LiPSs can be strengthened via the modification of carbon with heteroatom doping or with some polymers coating, the effects were still far from satisfactory [10,31–34]. Different from carbon hosts by physical entrapment, polar metal oxides/sulfides have shown improved binding ability towards LiPSs via chemical interactions and/or surface-mediated redox reactions, such as  $\text{MnO}_2$  [35,36],  $\text{TiO}_2$  [37–39],  $\text{MoS}_2$  [40,41],  $\text{WS}_2$  [42,43]. Thus, the lifespan of Li-S batteries was markedly prolonged due to the prominent suppression of LiPSs by intensive chemical interactions. However, the majority of these metal oxides/sulfides usually exhibit poor electrical conductivity, which is an impediment to the smooth conversion of chemically adsorbed LiPSs on the polar interface of hosts, giving rise to relatively lower sulfur utilization.

In this context, polar hosts with excellent conductivity are expected to afford efficient LiPSs adsorption and their reversible redox transformation. Intriguingly, transition metal nitrides (TMNs) and several oxygen-vacancy-enriched oxides have emerged as promising sulfur hosts with both polar nature and outstanding conductivity [44–46]. These TMNs, such as  $\text{TiN}$  [47,48],  $\text{Co}_4\text{N}$  [49],  $\text{VN}$  [50,51], delivered much stronger anchoring ability towards LiPSs and enabled the Li-S batteries with high sulfur utilization and improved cycling performances. As we know, these chemical interactions/affinities are mainly based on interfacial phenomena. That is to say, the interaction occurs at the contact interface between LiPSs and hosts [8]. Consequently, it can be envisaged that constructing increased exposed polar interfaces will render more intimate contact sites for efficient LiPSs immobilizing in these TMNs. While advances have been achieved to enhance the surface area of TMNs, there is still plenty of room for further exploring novel high-surface-area TMNs by constructing porous nanoarchitectures.

Herein, we propose template-assisted fabrication of mesoporous, conductive  $\text{Mo}_2\text{N}$  with high polar surface, which is used as sulfur host for Li-S batteries.  $\text{Mo}_2\text{N}$  with high surface area of  $121 \text{ m}^2 \text{ g}^{-1}$ , pore size of 8.6 nm and the conductivity of  $1 \times 10^5 \text{ S m}^{-1}$  was simultaneously achieved through a nanocasting strategy using mesoporous silica template and nitridation. This nanostructured  $\text{Mo}_2\text{N}$  has the following competitive advantages as sulfur host: 1) the high conductivity facilitates electron transfer for enhancing sulfur utilization; 2) the mesoporous skeletons within  $\text{Mo}_2\text{N}$  offer nanospaces for accommodation and physical confinement; 3) polar  $\text{Mo}_2\text{N}$ , especially mesostructured one, renders more exposed polar surface and intimate contact for efficiently binding LiPSs, thus suppressing their shuttling. Integrating mesopores into conductive and polar  $\text{Mo}_2\text{N}$  will contribute to the enhanced electrochemical performances of Li-S batteries. Impressively, the proposed  $\text{Mo}_2\text{N}$  host with sulfur delivered superior electrochemical performances in Li-S batteries, including higher capacity of  $995 \text{ mA h g}^{-1}$ , long cycling stability (91.9% capacity retention after 100 cycles), and reduced charge transfer resistance, superior to those of Nonporous- $\text{Mo}_2\text{N}/\text{S}$  and Mesoporous- $\text{MoO}_3/\text{S}$ .

## 2. Experimental

### 2.1. Synthesis of silica template

Mesoporous silica was synthesized via a soft templating approach [52]. In a typical synthesis, 6 g of Pluronic P123 ( $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$ ) was dissolved in 217 g of distilled water and 11.8 g of HCl (35 wt %). After that, 6 g of butanol was added into this solution under stirring at  $35^\circ\text{C}$  for 1 h. Subsequently, 12.9 g of tetraethylorthosilicate was added in one portion. The above mixture was stirred for 24 h at  $35^\circ\text{C}$ , followed by aging for 24 h at  $100^\circ\text{C}$  under static conditions. The as-prepared products were filtered, dried and calcined at  $500^\circ\text{C}$  for 3 h, yielding mesoporous silica.

### 2.2. Synthesis of Mesoporous- $\text{Mo}_2\text{N}$

Ammonium molybdate tetrahydrate, (AMT, 0.59 g) was dissolved in distilled water (4 mL). Afterwards, the above silica (1.0 g) template was added into the AMT solution, followed by ultrasonication for 20 min and stirring for 10 min. Then the obtained mixture was dried at  $70^\circ\text{C}$  overnight, calcined in air at  $450^\circ\text{C}$  for 3 h, obtaining  $\text{MoO}_3/\text{silica}$ . Then it was treated in  $\text{NH}_3$  at  $800^\circ\text{C}$  for 3 h to achieve  $\text{Mo}_2\text{N}/\text{silica}$ . After cooling down, the sample was washed by 50 mL 3% HF aqueous solution to remove the silica template. Finally, the black powder Mesoporous- $\text{Mo}_2\text{N}$  was achieved by filtration and drying. For comparison,  $\text{MoO}_3/\text{silica}$  was also treated with HF aqueous solution to yield mesoporous  $\text{MoO}_3$ , denoted as Mesoporous- $\text{MoO}_3$ . Meanwhile, nonporous  $\text{Mo}_2\text{N}$  (denoted as Nonporous- $\text{Mo}_2\text{N}$ ) was prepared by the similar procedure except the use of template.

### 2.3. Preparation of the sulfur composites

The Mesoporous- $\text{Mo}_2\text{N}/\text{S}$  composite was prepared via the typical melt-diffusion method. First, the required amount of sublimed sulfur and Mesoporous- $\text{Mo}_2\text{N}$  powder (1:1 in mass) were mixed thoroughly by grinding. Then the mixture was heated at  $155^\circ\text{C}$  for 12 h and cooled to room temperature. Nonporous- $\text{Mo}_2\text{N}/\text{S}$  and Mesoporous- $\text{MoO}_3/\text{S}$  composites were prepared following the same method.

### 2.4. Polysulfide adsorption

The  $\text{Li}_2\text{S}_6$  solution ( $2 \text{ mmol L}^{-1}$ ) was prepared by dissolving  $\text{Li}_2\text{S}$  and elemental sulfur with a stoichiometric molar ratio of 1:5 in 1,3-dioxolane (DOL) and 1,2-dimethoxyethane (DME) (1:1 v/v) and vigorous stirred at  $70^\circ\text{C}$ . 15 mg of  $\text{Mo}_2\text{N}$  or  $\text{MoO}_3$  was added into a glass vial containing 3 ml of the above  $\text{Li}_2\text{S}_6$  solution. A pristine  $\text{Li}_2\text{S}_6$  solution without adding any sample was used for comparison. All procedures were performed in an Ar-filled glovebox.

### 2.5. Material characterizations

The morphologies of the samples were investigated by FEI TF20 scanning electron microscope (SEM) and FEI Talos F200X transmission electron microscope (TEM) with an energy dispersive spectrometer (EDS) detector.  $\text{N}_2$  adsorption-desorption measurement was carried out using a Micromeritics ASAP 2020 analyzer at 77 K. The Brunauer-Emmett-Teller (BET) surface area was determined by BET theory. X-ray diffraction (XRD) patterns were recorded on a X'Pert PRO MPD (Cu K $\alpha$  radiation, 0.15406 nm) at room temperature. Ultraviolet/visible (UV) absorption spectroscopy was performed on lambda 35, Pekin Elmer Uv-vis spectrophotometer. The electrical conductivity was measured by a standard four-point-probe resistivity measurement system (ST2258C, Suzhou, China). Raman spectra analysis was conducted on Renishaw Invia RM200 (London, UK). Thermo-gravimetric analysis (TGA) was performed on a TGA/DSC 1/1600 (METTLER TOLEDO) instrument under Ar atmosphere from room temperature to  $600^\circ\text{C}$  at a heating rate

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