



# Complexing agent engineered strategy for anchoring SnO<sub>2</sub> nanoparticles on sulfur/nitrogen co-doped graphene for superior lithium and sodium ion storage

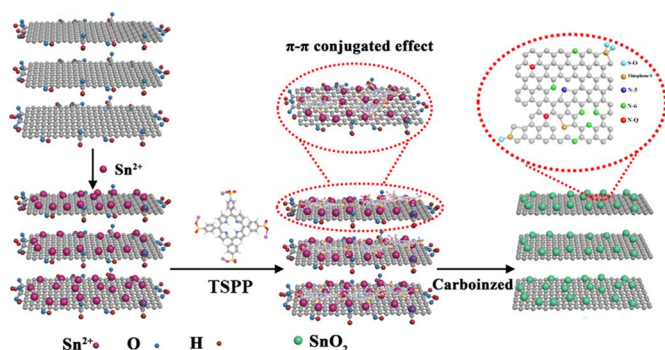


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## GRAPHICAL ABSTRACT

Porphyrin derivate can act as both the multi-heteroatom codoped source and the complexing agent to prepare sulfur/nitrogen co-doped graphene/SnO<sub>2</sub> composite, which shows high performance as anode materials for lithium and sodium ion batteries.



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## ABSTRACT

An effective strategy is proposed and developed to prepare sulfur/nitrogen co-doped graphene/SnO<sub>2</sub> composite (denoted SNGS). The key point of this strategy is the choice of heteroatom-containing organic compounds, 5, 10, 15, 20-tetra-(4-sulfonato phenyl) porphyrin (TSPP), which can act as both the multi-heteroatom codoped source and the complexing agent. After the calcination, the doped sulfur/nitrogen atoms could effectively pin SnO<sub>2</sub> nanocrystals on graphene sheets due to the existence of the binding effect. As a result, the unique feature as well as the synergetic effect between sulfur/nitrogen co-doped graphene and SnO<sub>2</sub> nanocrystals endows the composite materials with good electrochemical performances as anode materials for lithium ion batteries (LIBs) and sodium ion batteries (SIBs), including high initial discharge capacity (1089 mAh g<sup>-1</sup> at 50 mA g<sup>-1</sup> for LIBs and 673.8 mAh g<sup>-1</sup> at 25 mA g<sup>-1</sup> for SIBs) and reversible capacity (924.4 mAh g<sup>-1</sup> after 150 cycles for LIBs and 264.9 mAh g<sup>-1</sup> after 100 cycles for SIBs). The strategy derived from heteroatom-containing organic compounds might open new avenues for the design of high-performance doped graphene/metal oxide anode materials.

## 1. Introduction

As the most prospective candidates for energy storage devices,

lithium-ion batteries (LIBs) [1–5] and sodium-ion batteries (SIBs) [6–10] have attracted great interest in the scientific and industrial fields. By contrast, SIBs are recognized as sustainable alternatives to

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LIBs for large-scale energy storage systems due of the abundant resources and low cost of sodium [11–17]. In fact, for no matter what kind of rechargeable batteries, developing anode materials with the high specific capacity to meet the ever-growing performance demands is the most urgent task. In this regards, tin oxide ( $\text{SnO}_2$ ) has attracted considerable attention as potential substitutes for graphite because of high theoretical capacity, low cost, low toxicity, environmental benignity, and widespread availability [18–21]. Unfortunately, its large volume expansion during lithium/sodium ion insertion/extraction process leads to particle pulverization/exfoliation and rapid capacity fading, ultimately decreasing the cycling performance. Meanwhile,  $\text{SnO}_2$  also shows low electrical conductivity, which leads to poor rate capability. Taking into account the above two aspects, rationally designing nanostructured  $\text{SnO}_2$  and dispersing it into the electrically conductive carbon matrix seem to be the most feasible and applicable strategy.

Graphene, owing to the excellent conductivity, high surface area, pronounced chemical stability and high flexibility, has been widely used as the effective matrix for anchoring metal oxides to develop electrode materials for LIBs or SIBs [20,22–28]. Recently, continuous scientific endeavors have also been directed toward the synthesis of the doped graphene with heteroatoms such as nitrogen, boron and sulfur, which could potentially manipulate its electronic property and chemical reactivity as well as produce unexpected properties, such as large lithium/sodium ion storage capacity and high electrical conductivity [29–34]. Among various synthetic strategies of the doped graphene, using heteroatom-containing organic materials as the doped source seems to be the most applicable strategy [35–40]. It is well known that organic materials with the structural tunability contain different functional groups composed of multi-heteroatom, which can act as interfacial linkers to link graphene or graphene oxide by mutual electrostatic interactions and/or aromatic  $\pi$ - $\pi$  interaction, thus achieving the required single or multiple-heteroatom doped graphene. Moreover, the presence of organic materials with multi-heteroatom could act as the complexing agent for anchoring metal oxide nanoparticles, which could avoid the aggregation of metal oxide nanoparticles, thus achieving the formation of the well-distributed and small nanoparticles on the surface of the carbon matrix. In addition, this synthetic strategy avoids the requirement of toxic precursors, sophisticated equipment, special instruments, and/or rigorous conditions. Therefore, it is urgently required that adopting this strategy is to develop the multi-heteroatom codoped graphene as matrix to improve the performance of  $\text{SnO}_2$  as anode materials for LIBs or SIBs.

In this study, we present heteroatom-containing organic compounds derived method to synthesize sulfur/nitrogen co-doped graphene/ $\text{SnO}_2$  composite (denoted SNGS). It is well known that the molecular skeleton of organic compounds could contain different functional groups composed of multi-heteroatom, thus choosing suitable organic compounds is very important. Herein, 5, 10, 15, 20-tetra-(4-sulfonato phenyl) porphyrin (TSPP) was selected as both the multi-heteroatom codoped source and the complexing agent. On one hand, TSPP can be anchored on the surface of graphene oxide by the  $\pi$ - $\pi$  stacking and van der Waals forces and ultimately generating sulfur/nitrogen co-doped graphene. On the other hand, the coordinate interaction between  $\text{Sn}^{2+}$  and conjugate rings of TSPP molecules might generate the bonding effect, which could limit the agglomeration of  $\text{SnO}_2$  nanoparticles generated during calcination. Unexpectedly, the SNGS displays high electrochemical performance as anode materials for LIBs or SIBs.

## 2. Experimental

### 2.1. Synthesis of 5, 10, 15, 20-tetrakis(4-sodiosulfophenyl)-21H, 23H-porphyrin (TSPP)

5, 10, 15, 20-Tetraphenyl-21H, 23H-porphyrin (TPP) was synthesized by the Adlers method [41]. TPP (0.5 g, 0.8 mmol) was added into  $\text{H}_2\text{SO}_4$  (17 mL, 0.32 mol) and the mixture was stirred for 4 h at 120 °C.

After naturally cooling down to room temperature, the mixture was poured into 500 mL deionized water, then the pH of the solution was regulated to 8–9 by using NaOH (3 mol/L) and  $\text{NaHCO}_3$  (1 mol/L). Subsequently, the mixture solution was concentrated and filtered to remove the  $\text{Na}_2\text{SO}_4$ . Then the methanol was added into the as-obtained crude filtrate, and the mixture was filtered to remove the precipitated  $\text{Na}_2\text{SO}_4$ . Finally, the crude compound was recrystallized using methanol and acetone for three times to get the purified TSPP.  $^1\text{H-NMR}$  (400 MHz):  $\delta$  -2.92 (s, 2H), 8.06 (d,  $J$  = 7.7 Hz, 8H), 8.19 (m, 8H), 8.86 (s, 8H).

### 2.2. Synthesis of sulfur/nitrogen co-doped graphene/ $\text{SnO}_2$ composite (SNGS)

Graphene oxide (GO) used in this work was prepared by a modified Hummers method [42]. A homogeneous graphene oxide solution (5 g, 2 wt%) was dispersed into 15 mL deionized water by ultrasonication for 10 min, then  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  was added into the above GO solution and the mixture was ultrasonically dispersed for 30 min. Subsequently, 10 mL TSPP solution was poured into the above GO/ $\text{SnCl}_2$  solution by ultrasonication for another 30 min. After that, the mixed suspension was freeze-dried overnight, followed by thermal treatment at 600 °C for 3 h with the heating rate 3 °C/min under  $\text{N}_2$ . Herein, sulfur/nitrogen co-doped graphene/ $\text{SnO}_2$  composite was denoted as SNGS. In addition, graphene/ $\text{SnO}_2$  and sulfur/nitrogen co-doped graphene were also synthesized via the same procedure without adding the TSPP or  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ , which were denoted as GS and SNG, respectively.

### 2.3. Electrochemical tests

The working electrode was prepared by first mixing 80 wt% active material, 10 wt% acetylene black, 10 wt% polyvinylidene fluoride (PVDF) in appropriate amount of N-methyl-2-pyrrolidone (NMP as solvent), then covering the slurry on the Cu current collector. The loading density of the active material was ca. 1 mg  $\text{cm}^{-2}$ . For LIBs, lithium metal was used as the counter, Celgard 2400 membrane as the separator, and  $\text{LiPF}_6$  (1 M) in ethylene carbonate/dimethyl carbonate (EC/DMC 1:1 vol%) was used as the electrolyte. For SIBs, sodium metal was used as the counter and reference electrode, Celgard 2400 membrane as the separator, and 1 M  $\text{NaPF}_6$  in ethylene carbonate/dimethyl carbonate (EC/DMC, 1:1 v/v) as the electrolyte. The charge-discharge tests were carried out within a voltage range of 0.01–3.0 V on a Land Battery Measurement System (Land, PR China). Cyclic voltammetry (CV) and electrochemical impedance spectra (EIS) were conducted by a CS350 Electrochemical Workstation (Wuhan CorrTest Instruments Co., Ltd.).

## 3. Results and discussion

Fig. 1 outlines the synthesis process of SNGS. Firstly,  $\text{Sn}^{2+}$  ions could be absorbed on the surfaces of the GO sheet due to the electrostatic attraction between  $\text{Sn}^{2+}$  ions and oxygen containing groups from the GO nanosheets [43]. Subsequently, TSPP molecule is synthesized (the purity and identity of the compound was confirmed by  $^1\text{H}$  NMR spectroscopy as shown in Fig. S1) and then introduced into the mixture solution. The coordinate interaction between  $\text{Sn}^{2+}$  ions and conjugate rings of TSPP molecules as well as the  $\pi$ - $\pi$  stacking and van der Waals forces between TSPP molecules and GO allows TSPP molecules to be firmly absorbed on the GO sheets [44,45]. After the carbonization process, organic functional groups containing sulfur and nitrogen could act as heteroatom doped source and containing carbon could be decomposed to amorphous carbon,  $\text{Sn}^{2+}$  ions were translated into  $\text{SnO}_2$  and GO was reduced into graphene, thus sulfur/nitrogen co-doped graphene/ $\text{SnO}_2$  composite can be obtained. It should be pointed out that TSPP is selected as both the multi-heteroatom codoped source and the complexing agent. On one hand, the existence of sulfonic group

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