



# Reduced graphene oxide-wrapped pyrite as anode materials for Li-ion batteries with enhanced long-term performance under harsh operational environments



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## HIGHLIGHTS

- A facile route to rGO wrapped cauliflower-like FeS<sub>2</sub> microspheres has been provided.
- FeS<sub>2</sub>@rGO electrodes possessed outstanding performance under harsh environments.
- These attributes make FeS<sub>2</sub>@rGO particles promising candidate as anode materials.

## GRAPHICAL ABSTRACT

Cauliflower-like FeS<sub>2</sub> microspheres tightly wrapped by reduced graphene oxide (FeS<sub>2</sub>@rGO) have been synthesized by a facile and eco-friendly solution reaction route. Self-assembled mesostructured FeS<sub>2</sub> microspheres @rGO delivered excellent cycle stability, i.e. a remarkable reversible capacity of 1720 mAh g<sup>-1</sup> at a current density of 0.2 A g<sup>-1</sup> after 700 cycles at ambient temperature and an outstanding reversible capacity of 340 mAh g<sup>-1</sup> at a current density of 5.0 A g<sup>-1</sup> after 800 cycles as operated at an extreme temperature of 85 °C. All of these characteristics make FeS<sub>2</sub> microspheres@rGO promising anode materials for LIBs with ultra-long lifetimes and large energy density.



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## ABSTRACT

Cauliflower-like FeS<sub>2</sub> microspheres tightly wrapped by reduced graphene oxide (rGO-wrapped FeS<sub>2</sub>) have been synthesized by a facile and eco-friendly solution route. Self-assembled mesostructured FeS<sub>2</sub> microspheres wrapped by rGO delivered excellent cycle performances, i.e. a remarkable reversible capacity of 1720 mAh g<sup>-1</sup> at a current density of 0.2 A g<sup>-1</sup> after 700 cycles at ambient temperature and an outstanding reversible capacity of 340 mAh g<sup>-1</sup> at a current density of 5.0 A g<sup>-1</sup> after 800 cycles as operated at an extreme temperature of 85 °C. All of these characteristics of rGO-wrapped FeS<sub>2</sub> could be ascribed to artificially designed microstructure and gradual change of electrochemical reaction upon Li-cycling, making them promising anode materials for power batteries with ultra-long lifetimes and large energy density under harsh operational windows.

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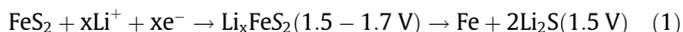
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## 1. Introduction

Lithium-ion batteries (LIBs) have played an increasingly important role in the daily lives of people due to their wide use in portable electronic devices and electrical vehicles based on their many outstanding features. Anode material is one of the most critical factors in improving electrochemical performance for LIBs. Unfortunately, commercial anode materials, mainly graphite, have severely limited the further enhancement of lithium storage performance for LIBs due to the low theoretical capacity of  $372 \text{ mAh g}^{-1}$  despite the fact that they are indeed cost effective and scalable. Therefore, exploration of novel anode materials of LIBs with large energy density becomes of great importance for meeting the growing requirements for large-power and heavy-duty applications. To date,  $\text{MS}_2$  ( $\text{M} = \text{Fe}, \text{Re}, \text{Co}, \text{and Mo}$  etc) have become very promising candidates for rechargeable batteries [1–4].

Iron pyrite ( $\text{FeS}_2$ ), an eco-friendly semiconductor composed of geologically abundant elements, has received significant attention because of its high theoretical capacity of  $890 \text{ mAh g}^{-1}$ , low cost and environmental benignity. In fact,  $\text{Li}/\text{FeS}_2$  batteries have already commercialized as primary batteries since they possess obvious advantages in high capacity and long life expectancy [5]. However, the severe capacity fading caused by the electrochemical pulverization during charge/discharge cycling hinders their utilization as anode materials in rechargeable lithium-ion batteries. It is much in evidence that there are still some intrinsic problems ahead of us to be solved for possible applications in rechargeable batteries for pyrite.

It is generally accepted that pyrite ( $\text{FeS}_2$ ) follows an intercalation/conversion mechanism to store lithium during Li cycling (Eq. (1)) [5].



Obviously, root cause of drastic volume change was the conversion reaction triggered at  $\sim 1.5 \text{ V}$ . Several strategies have been accordingly adopted to avoid the resulting electrode failure. A commonly-utilized approach is formation of rationally architected hybrids containing  $\text{FeS}_2$  and advanced carbon materials, where robust accommodation capability and excellent conductivity of carbon materials become of crucial importance to enhancing electrochemical performance of active materials. A pertinent measure for the particular  $\text{FeS}_2$  material system is the control of cut-off voltage ( $1.0\text{--}3.0 \text{ V}$ ), which can partially suppress the occurrence of conversion reaction for the micro-sized  $\text{FeS}_2$  materials and accordingly preserve the integrity of electrodes [6–12]. Very recently,  $\text{FeS}_2$ @carbon fiber electrode demonstrated energy density of  $840 \text{ Wh kg}^{-1}$  at  $200 \text{ mA g}^{-1}$  after 100 cycles in the voltage range of  $1.0\text{--}3.0 \text{ V}$  (vs  $\text{Li}/\text{Li}^+$ ) [10], and in another reference, core-shell  $\text{FeS}_2$ @N-doped graphene delivered a specific capacity of  $\sim 400 \text{ mAh g}^{-1}$  after 400 cycles at  $0.5 \text{ A g}^{-1}$ , with capacity fading of  $\sim 0.9 \text{ mAh g}^{-1}$  per cycle [13]. However, the increase in lower limit of voltage inevitably leads to a declined reversible capacity and consequently offsets inherent high capacity advantage of pyrite to some extent; more unacceptably, conversion reaction could not be completely hindered yet because of extremely close potential (at  $\sim 1.5 \text{ V}$ ) where both intercalation and conversion reaction were almost simultaneously triggered.

Another route to improve electrochemical performance of  $\text{FeS}_2$ -based materials was artificial synthesis of nanostructured particles to accommodate the volume change during Li-cycling [14,15], because such a nanostructured anodic material afforded high cycling energy efficiency, increased safety, high power density and extended lifetimes [5,16–18]. Note that nanostructured particle really allowed for the wider discharge/charge window ( $0.01\text{--}$

$3.0 \text{ V}$  vs  $\text{Li}/\text{Li}^+$ ) [14,15,19]. As reported by Li et al. [20], carbon nanotube-encapsulated  $\text{FeS}_2$  nanoparticles delivered a reversible capacity of  $800 \text{ mAh g}^{-1}$  at a current density of  $0.2 \text{ A g}^{-1}$  after 200 cycles. In another sample,  $\text{FeS}_2$ @S-C sample also afforded a reversible capacity of  $689 \text{ mAh g}^{-1}$  after 100 cycles at a low current density of  $0.1 \text{ A g}^{-1}$  [19]. However, it appeared to be a formidable difficulty in simultaneously acquiring the high reversible capacity, strong cycling stability and long-term lifetime for  $\text{FeS}_2$ -based electrodes under large current density for the above-mentioned examples.

Because three-dimensional structure of  $\text{FeS}_2$ -containing hybrids exerts great influence on the electrochemical performance of resulting electrodes, several morphologies of pyrite such as nanocrystal [21], microspheres [15], hollow microspheres [22], nanowires [23], and porous particles [24] have been synthesized to match with carbon such as graphene (reduced graphene oxide) [14,15], CNT [6], carbon black [25,26], or carbon fiber [10]. However, rational design of three-dimensional microstructure for pyrite via a facile, scalable and eco-friendly route, enabling the  $\text{FeS}_2$ -based materials to possess an excellent lithium insertion/extraction property in wider potential window, is highly desirable while the challenge is enormous.

In present research, we provided a solution-phase route to reduced graphene oxide (rGO)-wrapped cauliflower-like  $\text{FeS}_2$  composites, which were subsequently utilized in lithium-ion batteries with unprecedented performance. The deliberately designed mesoporous architecture of  $\text{FeS}_2$  possessed more lithium storage sites and Li-ion diffusion channels, greatly facilitating full wettability of the carbonate solvent in the electrolyte and accelerating deintercalation of Li-ions. And while maintaining the above characteristics of nanoparticles, self-assembled mesoporous  $\text{FeS}_2$  particles have an obvious advantage of high tap density, resulting in the enhanced volume energy density. More interestingly, rGO in composites not only leads to an excellent conductivity and fast electron transportation, but also acts as a buffer to accommodate the volume expansion, maintains structural consistency and further prevents electrodes from deteriorating. As a consequence, rGO-wrapped cauliflower-like  $\text{FeS}_2$  particles delivered an unprecedented reversible capacity of  $1720 \text{ mAh g}^{-1}$  after 700 cycles at a current density of  $0.2 \text{ A g}^{-1}$  at ambient temperature, particularly, an outstanding reversible capacity of  $340 \text{ mAh g}^{-1}$  at a current density of  $5.0 \text{ A g}^{-1}$  after 800 cycles as operated at an extreme temperature of  $85 \text{ }^\circ\text{C}$ . More importantly, the similar electrochemical mechanism for  $\text{FeS}_2$ @rGO to store Li-ion in an everchanging temperature environment has been confirmed. Those distinct identities make  $\text{FeS}_2$ @rGO promising anode materials for power batteries operated under ultrawide operational window.

## 2. Experimental section

### 2.1. Preparation of rGO-wrapped mesoporous $\text{FeS}_2$ composites

RGO-wrapped mesoporous  $\text{FeS}_2$  powders were synthesized through a facile solution reaction. In a typical process,  $3 \text{ mmol Na}_2\text{S}\cdot 9\text{H}_2\text{O}$  and  $3 \text{ mmol}$  pure sulfur powders were magnetically stirred in  $40 \text{ mL}$  de-ionized water in a beaker to form a yellow-brown solution. Graphene oxide was prepared by a modified Hummer method [27], then ultrasonically exfoliated for  $2 \text{ h}$  to obtain uniform graphene oxide dispersion.  $0.09 \text{ g}$  above-exfoliated graphene oxide was mixed with  $3 \text{ mmol FeSO}_4\cdot 7\text{H}_2\text{O}$  in  $20 \text{ mL}$  deionized water containing  $0.09 \text{ g}$  ascorbic acid. Finally, solution comprising of graphene oxide and  $\text{Fe}^{2+}$  was merged with aforementioned yellow-brown solution under vigorous stirring and refluxed  $1 \text{ h}$  at  $\text{N}_2$  atmosphere to gather black precipitate. After naturally cooling down to room temperature, the precipitate was rinsed three

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