# Graphene-encapsulated cobalt sulfides nanocages with excellent anode performances for lithium ion batteries

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## ARTICLE INFO

## ABSTRACT

A layer-by-layer assembled composite of graphene nanosheets (GNSs) wrapped monodisperse cobalt sulfides ($CoS_2$) nanocages has been prepared via a solvothermal method. The flexible GNSs in the layered composite act as the effective matrix to encapsulate the monodisperse $CoS_2$ nanocages, buffer the volume changes and prevent the aggregation of the $CoS_2$ nanocages during electrochemical cycling. The loosely stacked GNSs, which are induced with the insertion of $CoS_2$, are convenient for electrolyte wetting and serve as highway for the rapid electron and lithium transport. The monodisperse nanocages can supply additional space to tolerate the volume changes, shorten lithium diffusion path, and do not tend to aggregate. As a result, the specific sample can deliver a high capacity approaching $800 \, \text{mA h g}^{-1}$ after 150 cycles at $100 \, \text{mA g}^{-1}$ and $697 \, \text{mA h g}^{-1}$ after 300 cycles at $500 \, \text{mA g}^{-1}$, in addition to good capacity retention and excellent rate capability, making it a promising candidate as next-generation anode materials for lithium-ion batteries.

## 1. Introduction

To meet the increasing demands for high-performance lithium-ion batteries (LIBs), there is a desirable requirement of exploring next-generation anode materials with higher capacity, better cyclic stability, and better rate capability to replace the traditional graphite anode. Inspired by the report of some transition metal oxides with highly reversible conversion reactions by Tarascon's group [1], the widespread research interests have been aroused. These materials, however, usually suffer from rapid capacity fading, limited cycling life, and poor high-rate performance because of the intrinsic volume effect and poor conductivity of transition metal oxides [2]. To address these problems, many efforts have been triggered to improve the electrochemical lithium storages of these oxides in recent years. Stable and fast lithium storages could be achieved for oxides by using nanostructured materials. Specially, hollow or porous nanostructures are of particular benefit because they possess well-defined interior voids to allow volume variation and shortened charge transfer path, both of which can undoubtedly lead to improved electrochemical

lithium storage performance [3–10]. Another specifically effective solution to improve the cycling stability and rate performance of oxide anodes is to fabricate composites of oxides with carbon materials, assigning to the fruitful buffering effect of carbon materials as well as their good electronic conductivity [11–16]. Considering the intriguing features of robust structure, large surface area, good electrical and thermal conductivity, charge transport mobility, and good chemical stability [17,18], graphene is particularly considered as a promising buffering matrix [19–24]. During the long-term repeated cycling, the flexible graphene nanosheets (GNSs) can not only accommodate the volume variation but also prevent the particles from aggregating.

Similar to oxides, metal sulfides possess high theoretical capacities via the conversion reactions, and they are receiving increasing research interest as the promising alternative anode materials [25–30]. Among them, cobalt sulfides have attracted great attention, and valuable efforts have been made to demonstrate their potential applications as LIBs anode materials [31–39]. With the aim to promote their practical applications, many strategies have been developed to improve the electrochemical performance of cobalt sulfides based anode, such as nanostructuring, carbon-coating, and employing graphene as the support matrix. For instance, $CoS_2$ hollow spheres prepared by Wang et al. deliver a high initial capacity of $850 \, \text{mA h g}^{-1}$ and retain the

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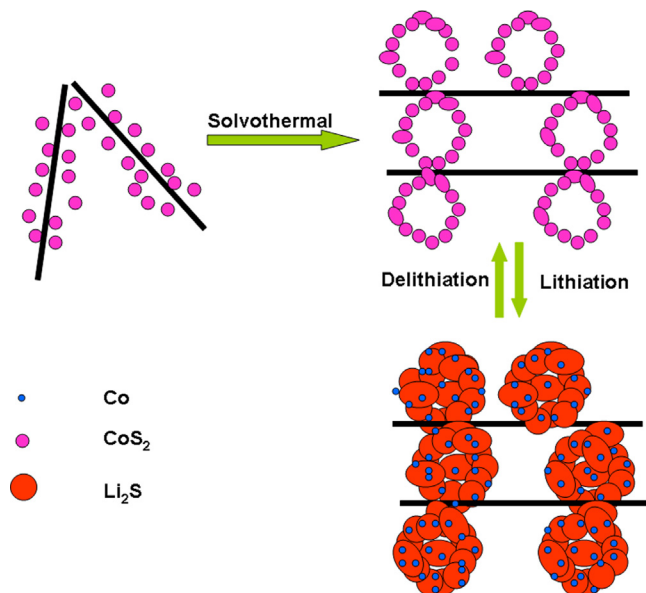E-mail address: zhx1213@126.com (X. Zhang).

capacity of 320 mA h g$^{-1}$ after 40 cycles [34]. The capacity of CoS$_2$@carbon decreases from ~900 mA h g$^{-1}$ at the 1st cycle to 440 mA h g$^{-1}$ after 50 cycles [35]. Su et al. reveal the lithiation progress of CoS$_2$ particles with the aid of in situ TEM observation technique and demonstrate that, graphene substrate can alleviate the volume expansion and prevent the particles cracks, leading to improved cycling stability [38]. So far, the most excellent performance is obtained from the complicated phases of cobalt sulfides anchored graphene composite, which show a capacity of ~1018 mA h g$^{-1}$ at the 1st cycle and a high capacity of 950 mA h g$^{-1}$ after 50 cycles [39]. Although these cobalt sulfides nanostructures and/or cobalt sulfide based composite materials exhibit high capacities up to 1000 mA h g$^{-1}$, their cycling stability is still restricted with lifespan rarely beyond 50 cycles and their electrochemical performances are mainly obtained at low current density (<100 mA g$^{-1}$), which cannot meet the requirement of practical use in LIBs. So it is desirable to exploit novel cobalt sulfides based anode materials that possess stable and fast reversible lithium storage properties.

In this work, layer-by-layer self-assembled graphene sheets enwrapped monodisperse CoS$_2$ nanocages composite (CoS$_2$/G) is firstly prepared through a one-pot solvothermal procedure (Scheme 1). As shown in Scheme 1, the interleaved network of GNSs can not only supply 3D tunnels for fast electrical and lithium conductivity but also buffer the large volume changes of CoS$_2$ nanocages and prevent their aggregation during the electrochemical cycles. The nanosized, monodispersed CoS$_2$ nanocages can shorten the lithium transport path and offer additional space to accommodate the volume expansion. So boosted by the synergistic effect between the specific nanocage features and the layered GNSs support, the excellent electrochemical performance, especially the fast and stable lithium storage property and prolonged lifespan, is observed when the sample is tested as the anode.

## 2. Experimental

### 2.1. Sample preparation

CoCl$_2$·6H$_2$O, CH$_4$N$_2$S, ethylene glycol are of analytical grade and purchased from Sinopharm Chemical. Graphene oxides (GO) is synthesized with the modified Hummers method as reported elsewhere previously [40]. For preparation of CoS$_2$/G, 2 m mol CoCl$_2$·6H$_2$O and 4 m mol CH$_4$N$_2$S are dissolved into 30 mL ethylene glycol. Then it is poured into 30 mL of GO aqueous dispersion (5 mg mL$^{-1}$). After ultrasonic for 10 min, the resultant mixture is transferred into 80 mL Teflon-lined autoclave and maintained at 160 °C for 24 h. The products are harvested with centrifugation and then washed with absolute ethanol for vacuum drying at 60 °C for 24 h. Then it is loaded into a tube furnace for calcination at 400 °C in Ar atmosphere for 5 h.

### 2.2. Materials characterization

The sample is characterized with powder X-ray powder diffraction (XRD, Philips X'-pert X-ray diffractometer, Cu Kα radiation: λ = 0.154056 nm), confocal microprobe Raman system (LabRam-010, 632 nm as excitation source), scanning electron microscope (SEM, JEOL JSM-7500F scanning electron microscope), and transmission electron microscope (TEM, JEOL JEM-2100). The thermogravimetric analysis (TGA) is measured on a TG2091F from room temperature to 650 °C with a heating rate of 10 °C min$^{-1}$ in air.

The cells are disassembled after the electrochemical charge-discharge test. The CoS$_2$/G electrode materials are scraped from the working electrodes and rinsed with 1-methyl-2-pyrrolidinone for SEM and TEM characterization.

### 2.3. Electrochemical test

The electrochemical characterizations of the products are performed using a CR2016-type coin cell. The working electrode is made by compressing a mixture of 85 wt% CoS$_2$/G, 5 wt% acetylene black and 10 wt% polyvinylidene fluoride (PVDF) onto a copper foil current collector. The electrode is dried at 100 °C for 24 h in vacuum oven. The cell is assembled in a glove box filled with high pure argon using metallic lithium sheet as negative electrode and the Clegard 2300 microporous film as separator. The electrolyte is 1 M LiPF$_6$ dissolved in a mixture of ethylene carbonate (EC)/dimethyl carbonate (DMC)/ethyl methyl carbonate (EMC) (1:1:1 in volume) (Zhangjiagang, China). The cells are charged and discharged at various rates between 3 and 0.01 V using a LAND CT2001A Battery Cycler (Wuhan, China). Cyclic voltammetry (CV) measurements are conducted using a three-electrode cell and metallic lithium is used as both the counter and reference electrode. The experiments are recorded on a CHI660A (CH Instruments, Shanghai, China) over the potential range from 0.01–3.0 V vs. Li$^+$/Li at a scanning rate of 0.05 mV s$^{-1}$.

## 3. Results and discussion

XRD is performed to record the crystal structure and phase purity of CoS$_2$/G. As is shown in Fig. 1(a), the dominant diffraction peaks can be indexed to cubic CoS$_2$ with space group *Pa*3 (JCPDS No. 41-1471). The typical diffraction peak (0 0 2) of graphene is detected at 2θ = 25.9°, indicating the reduction of graphene oxides into graphene through the solvothermal procedure. Additionally, minor CoS diffraction peaks are also observed in the XRD patterns, suggesting that there is trace amount of CoS in the CoS$_2$/G composite. Raman spectra of GO and CoS$_2$/G are shown in Fig. 1b. The D/G intensity ratio of CoS$_2$/G (1.23) is significantly higher than the value of 0.91 for GO. One reason for this phenomena should be the reduction of GO [37,39,40]. Another contribution is the partial insertion of embedded particles between graphene sheets in the layer-by-layer self-assembled structures [36,39]. In the Raman spectra of CoS$_2$/G, an additional peak located at ~400 cm$^{-1}$ is observed, corresponding to the A$_g$ modes of CoS$_2$ [41].



**Scheme 1.** The synthesis process and repeated electrochemical lithiation-delithiation cycles of CoS$_2$/G.