



# Carbon encapsulated cobalt sulfide nano-particles anchored on reduced graphene oxide as high capacity anodes for sodium-ion batteries and glucose sensor



Vadahanambi Sridhar<sup>a</sup>, Hyun Park<sup>a, b, \*</sup>

<sup>a</sup> Global Core Research Center for Ships and Offshore Plants (GCRC-SOP), Pusan National University, Busan 46241, Republic of Korea

<sup>b</sup> Department of Naval Architecture and Ocean Engineering, Pusan National University, Busan 46241, Republic of Korea

## ARTICLE INFO

### Article history:

Received 22 November 2017

Received in revised form

7 June 2018

Accepted 9 June 2018

### Keywords:

Cobalt sulfide

Graphene

Encapsulation

3D nano architectures

Sodium ion battery

Glucose sensor

## ABSTRACT

Cobalt sulfide is a promising anode material for a sodium-ion battery because of its high capacity and abundance. However, practical issues such as huge volume changes during sodiation/desodiation result in a low capacity retention during cycling, thus posing a serious challenge to practical applications. In this work, we report a rather easy, single pot microwave synthesis technique having the ability to create carbon-coated, uniformly distributed cobalt sulfide nanoparticles (20–40 nm) on reduced graphene oxide (CoS<sub>2</sub>@C-rGO). In this structure, the graphene substrate acts as a robust conductive platform to anchor cobalt sulfide, and the outer carbon encapsulation guarantees both the structural integrity and conductivity of the composite. When evaluated as an anode material in a sodium-ion battery, CoS<sub>2</sub>@CrGO exhibited a stable cycling performance and superior high-rate capability, delivering a reversible capacity as high as 794.9 mAhg<sup>-1</sup> at 0.5 A, after 175 cycles. Furthermore, our CoS<sub>2</sub>@C-rGO electrodes can be used as enzyme-less glucose sensors that exhibit a wide linear response within a range of up to 3 mM of glucose and a low detection limit of 0.078 M.

© 2018 Elsevier B.V. All rights reserved.

## 1. Introduction

The rapidly increasing application of lithium ion batteries (LIBs), ever since their commercialization by Sony in 1991, has increased the demand for lithium, the price of which has doubled in the last five years. This has prompted researchers to search for “beyond lithium” batteries. Amongst the non-lithium secondary ion batteries, such as batteries based on K<sup>+</sup>, Mg<sup>2+</sup>, and Al<sup>3+</sup>, sodium ion batteries (SIBs), which work on the principle of shuttling Na<sup>+</sup>, are drawing increasing attention, particularly in applications such as large-scale static energy storage systems. When compared with lithium, sodium is more abundant, more uniformly distributed, less expensive, and environmentally benign. However, the relatively large size of the sodium ion when compared with lithium (+82% at the atomic scale and +55% for the ion), and its tendency to form NaC<sub>186</sub> (as compared to LiC<sub>6</sub>) during an electrochemical reaction with carbon anodes, results in typical carbon-based sodium ion

batteries (SIBs) operating at less than 50% of the capacity of a typical LIB. The large size of the Na<sup>+</sup> ion leads to sluggish diffusion kinetics in the electrodes and electrolytes, thereby limiting the direct applicability of traditional LIB anode materials to SIBs. The most commonly used SIB anodes could be divided into three broad categories: those which work on the principle of *intercalation*, such as carbon-based nanostructures; those which are anodes of the *alloying* type, such as transition metal compounds (TMC); and hybrids of the first two types, such as anodes composed of metal-decorated graphene. Similar to LIB technology, the most common intercalation anodes in SIBs are carbonaceous materials such as hard carbons [1], hetero-atom doped carbons [2], exfoliated graphite [3], graphene [4], carbon nanotubes (CNT) [5], and graphene-CNT hybrids [6]. Amongst the many TMC-based alloying type anodes, the applicability of oxides [7–9], phosphides [10], carbides [11], and sulfides [12–14] has been reported. The applicability of cobalt sulfides should be specially mentioned owing to their high electrical conductivity. Cobalt sulfides are used not only in energy storage and generation devices such as sodium [15–17] and lithium-ion batteries [18,19], super-capacitors [20,21], and photo-voltaic solar cells [22], but also as enzyme-less glucose sensors [23,24]. The variable solubility of sulfur in cobalt results in

\* Corresponding author. Global Core Research Center for Ships and Offshore Plants (GCRC-SOP), Pusan National University, Busan 46241, Republic of Korea.

E-mail address: [hyunpark@pusan.ac.kr](mailto:hyunpark@pusan.ac.kr) (H. Park).

numerous stoichiometries, which lead to the formation of cobalt sulfides in multi-valent states, as in the  $\text{Co}_4\text{S}_3$  [25],  $\text{Co}_9\text{S}_8$  [26],  $\text{CoS}$  [27],  $\text{Co}_3\text{S}_4$  [28],  $\text{Co}_2\text{S}_3$ , and  $\text{CoS}_2$  phases. Furthermore, by modifying the synthesis conditions, nanostructured cobalt sulfides with various shapes can be obtained, including nanoneedles [29], nanotubes [30], nanoparticles [31], nanometer-thick platelets [32], and nanowires [33]. However, when applied as anodes in SIBs, pristine cobalt sulfide undergoes a large volumetric expansion upon sodiation/desodiation, resulting in a very poor rate ability and low capacity retention during cycling. To overcome these practical problems, researchers have developed two strategies. The first strategy is to minimize the sodiation-induced volumetric expansion/contraction of cobalt sulfide by encapsulating it in a functional carbon matrix. The second strategy is synthesizing mesoporous three-dimensional (3-D) cobalt sulfide frameworks that provide sufficient 'free space' to accommodate possible volumetric changes. With respect to the mentioned strategies, there are reports on the synthesis of cobalt sulfide nanoparticles anchored on CNT [34], reduced graphene oxide sheets decorated with cobalt sulfide nanoparticles [35], hollow cobalt sulfide microspheres [36], etc. Though these techniques have resulted in some improvement of the electrochemical performance, the synthesis condition generally involves multiple steps, and the performance is still much less than the theoretical capacity of cobalt sulfide. Therefore, there is a need for a one-step rational synthesis of cobalt sulfide-based electrodes, which can deliver the full theoretical sodium ion capacity. Herein we report a novel and a rather easy technique to synthesize carbon encapsulated cobalt sulfide core-shell nanoparticles anchored on reduced graphene oxide ( $\text{CoS}_2@\text{C-rGO}$ ), using a simple microwave technique with starting materials of graphene oxide, cobalt acetate, and thioacetamide. The applicability of the synthesized  $\text{CoS}_2@\text{C-rGO}$  as anode materials for sodium ion batteries and enzyme-less glucose sensors is also investigated.

## 2. Experimental

### 2.1. Materials and methods

Reagent-grade cobalt acetate and thioacetamide was purchased from Sigma–Aldrich, and the materials were used as received. Graphene oxide was synthesized using Tour's method [37]. The morphological characterization of the nanostructures was carried out by field-emission scanning electron microscopy (FE-SEM, Nova NanoSEM 230 FEI operating at 10 kV, with no metal coating applied to the samples). Moreover, high resolution transmission electron microscope (HRTEM) micrographs and energy dispersive x-ray spectroscopy (EDX) elemental maps were recorded using a JEM3011HR microscope operated at 200 kV, and a holey-carbon-coated copper grid. The chemical analysis was performed by X-ray photoelectron spectroscopy (Sigma Probe Thermo VG spectrometer using Mg  $K\alpha$  X-ray sources). The XPS spectra were curve-fitted with a mixed Gaussian–Lorentzian shape, using the freeware XPSPEAK version 4.1. A thermal gravimetric analysis was performed in a TA Instruments Q600 SDT thermal analyzer with a sample size of approximately 10 mg, over a temperature range of 25–800 °C, at a heating rate of 10 °C  $\text{min}^{-1}$  in air.

### 2.2. Synthesis of $\text{CoS}_2@\text{C-rGO}$

A single pot technique was used to synthesize  $\text{CoS}_2@\text{C-rGO}$ . A 0.4 mg/mL aqueous solution of graphene oxide was synthesized using a modified Tour method (representative SEM and TEM images are shown in Figs. S1 and S2 of the supplementary information). Furthermore, 2 g of cobalt acetate and 4 g of thioacetamide were sequentially added, and the solution was sonicated in an

ultrasonic bath operating at 600 W for 60 min. This solution was then placed in an oven, heated to 100 °C to evaporate the water, and the resultant viscous mixture was transferred to a glass vial and subjected to microwave irradiation at 700 W for 120 s, forming a powdery solid.

### 2.3. Sodium-ion battery testing

Electrochemical tests were conducted using CR2032 coin-type test cells assembled in an argon-filled glove box. Working electrodes were prepared with active materials and polyacrylic acid as the binder (at a mass ratio of 85:15). These materials were added to ethanol and mixed into a homogeneous slurry. The slurry was cast onto a glass plate cleaned with piranha solution, and dried in a vacuum for 5 h at 100 °C. The coin cells were assembled using pure sodium foil as a counter electrode, a glass fiber as the separator, and 1 M  $\text{NaClO}_4$  in an ethylene carbonate/propylene carbonate mixture (1:1 v/v) as the electrolyte. The working electrodes were composed of 0.5 g of active material and a sodium foil separated by a microporous Celgard 2400 membrane. Galvanostatic charge–discharge cycling tests were performed within the 0.001–3 V voltage range, using a WBCS 3000, Won-A-Tech, Korea battery testing system.

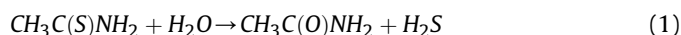
### 2.4. Preparation of $\text{CoS}_2@\text{C-rGO}$ modified FTO electrodes

A layer-by-layer approach was used to fabricate  $\text{CoS}_2@\text{C-rGO}$ -FTO (fluorine-doped tin oxide) electrodes for glucose sensing. In the first step, the FTO substrate was cleaned by sonication in acetone, then distilled water, and then concentrated NaOH in 1:1 (v/v) water/ethanol and distilled water for 10 min. Thereafter, it was dried in an oven under a stream of  $\text{N}_2$  gas. Furthermore, 0.1 gm of  $\text{CoS}_2@\text{C-rGO}$  was dispersed in 10 mL of DMP and was spin-coated on a pre-cleaned FTO substrate at 4000 rpm for 60 s. A total of five layers were deposited on the FTO substrate, which was then annealed at 100 °C for 180 min in a stream of  $\text{N}_2$  gas.

## 3. Results and discussion

### 3.1. $\text{CoS}_2@\text{C-rGO}$ anodes

The morphology of the  $\text{CoS}_2@\text{C-rGO}$  was studied in two modes: the 'in-lens' mode to gather surface information, and the back-scattered electron (BSE) image mode to study compositional differences. The representative microstructure, is studied using the 'in-lens' mode of SEM at low and high magnifications, as exhibited in Fig. 1(a) and (b). These figures reveal well-dispersed spherical nanostructures that are evenly distributed on the reduced graphene oxide (rGO) substrate. In the corresponding BSE image (Fig. 1(c)), the morphology is dominated by bright  $\text{CoS}_2$  nanoparticles, which reflect more electrons owing to their higher atomic weight. Moreover, the electron-transparent carbon moieties of the rGO substrate and carbon shells are not visually discernible. The  $\text{CoS}_2$  nanoparticle formation mechanism, through the reaction of thioacetamide, can be explained using two different scenarios. In the first scenario, when thioacetamide is added to an aqueous solution of graphene oxide and cobalt, thioacetamide decomposes to  $\text{H}_2\text{S}$  and acetamide due to the following hydrolysis reaction [38]:



The cobalt cations react with the  $\text{H}_2\text{S}$ , forming cobalt sulfide nanoparticles, whereas the acetamide byproducts formed during the hydrolysis reaction undergo catalytic dehydrogenation to form cyanuric acid, which reduces graphene oxide to graphene [39]. In the second scenario, cobalt ions directly react with thioacetamide

Download English Version:

<https://daneshyari.com/en/article/7990688>

Download Persian Version:

<https://daneshyari.com/article/7990688>

[Daneshyari.com](https://daneshyari.com)