



# Capacitive properties of reduced graphene oxide microspheres with uniformly dispersed nickel sulfide nanocrystals prepared by spray pyrolysis



Su Min Lee <sup>a,1</sup>, You Na Ko <sup>b,1</sup>, Seung Ho Choi <sup>b</sup>, Jong Hwa Kim <sup>c</sup>, Yun Chan Kang <sup>b,\*</sup>

<sup>a</sup> Department of Chemical Engineering, Konkuk University, 1 Hwayang-dong, Gwangjin-gu, Seoul 143-701, Republic of Korea

<sup>b</sup> Department of Materials Science and Engineering, Korea University, Anam-Dong, Seongbuk-Gu, Seoul 136-713, Republic of Korea

<sup>c</sup> Daegu center, Korea Basic Science Institute, 80 Daehakro Bukgu, Daegu 702-701, Republic of Korea

## ARTICLE INFO

### Article history:

Received 22 January 2015

Received in revised form 24 March 2015

Accepted 27 March 2015

Available online 28 March 2015

### Keywords:

graphene composite

nickel sulfide

lithium ion battery

anode material

spray pyrolysis

## ABSTRACT

Nickel sulfide-reduced graphene oxide (RGO) composite powders with spherical shapes are prepared by a one-pot spray pyrolysis process. The optimum mole ratio of nickel nitrate and thiourea to obtain nickel sulfide-RGO composite powders with high initial capacities and good cycling performance is 1:8. The bare nickel sulfide and nickel sulfide-RGO composite powders prepared directly by spray pyrolysis have mixed crystal structures of hexagonal  $\alpha$ -NiS and cubic Ni<sub>3</sub>S<sub>4</sub> phases. The bare nickel sulfide powders are prepared from the spray solution without graphene oxide sheets. The nickel sulfide-RGO composite powders have sharp mesopores approximately 3.5 nm in size. The discharge capacities of the nickel sulfide-RGO composite powders for the 1st and 200th cycles at a current density of 1000 mA g<sup>-1</sup> are 1046 and 614 mA h g<sup>-1</sup>, respectively, and the corresponding capacity retention measured from the second cycle is 89%. However, the discharge capacities of the bare nickel sulfide powders for the 1st and 200th cycles at a current density of 1000 mA g<sup>-1</sup> are 832 and 16 mA h g<sup>-1</sup>, respectively. The electrochemical impedance spectroscopy (EIS) measurements reveal the high structural stability of the nickel sulfide-RGO composite powders during cycling.

© 2015 Elsevier Ltd. All rights reserved.

## 1. Introduction

Nickel sulfides with various compositions, such as NiS, NiS<sub>2</sub>, Ni<sub>3</sub>S<sub>2</sub>, Ni<sub>6</sub>S<sub>5</sub>, Ni<sub>7</sub>S<sub>6</sub>, and Ni<sub>3</sub>S<sub>4</sub>, have been applied as energy storage materials [1–6]. Nanostructured bare nickel sulfide and nickel sulfide-carbon composite materials have been developed to improve the electrochemical properties of the nickel sulfide materials by tolerating the morphological change during cycling [4]. Nickel sulfide-graphene composite materials in particular have been applied as anode materials for lithium ion batteries (LIBs). Graphene materials can be effectively applied to overcome problems such as the low conductivity and large volume change of the active materials during cycling. Zhu et al. fabricated Ni<sub>3</sub>S<sub>2</sub> nanoparticles wrapped with in situ-generated N-doped graphene sheets (Ni<sub>3</sub>S<sub>2</sub>@N-G) [5]. Ni<sub>3</sub>S<sub>2</sub>@N-G exhibited a highly improved reversible capacity, as well as excellent cycling performance and rate performance as an anode material for LIBs. Mahmood et al.

prepared a phase-controlled Ni<sub>3</sub>S<sub>4</sub>/N-doped graphene composite through a hydrothermal method [6]. The Ni<sub>3</sub>S<sub>4</sub>/N-doped graphene composite materials annealed at 250 °C showed high discharge capacity and an excellent capacity retention of 95% after the 100th cycle at 4 C.

The electrochemical properties and morphologies of the metal sulfide-graphene composite materials are strongly affected by their preparation processes. Therefore, various solution-based processes, such as hydrothermal, solvothermal, precipitation, and sol-gel processes, have been applied to prepare the metal sulfide-graphene composite materials for energy storage [7–13]. Recently, metal oxide-reduced graphene oxide (RGO) and metal sulfide-carbon composite materials were successfully prepared by a simple spray pyrolysis process, which is one of the gas-phase reaction methods [14–20]. The composite materials, with spherical fine-sized particles prepared by a one-pot spray pyrolysis process, had high initial capacities and good cycling performance. However, to the best of our knowledge, the preparation of nickel sulfide-RGO composite materials by spray pyrolysis has not been studied.

In this study, nickel sulfide-RGO composite materials with spherical particles were prepared by a one-pot spray pyrolysis process from a colloidal spray solution containing dispersed

\* Corresponding author.

E-mail address: [yckang@korea.ac.kr](mailto:yckang@korea.ac.kr) (Y.C. Kang).

<sup>1</sup> These authors contributed equally to this work.

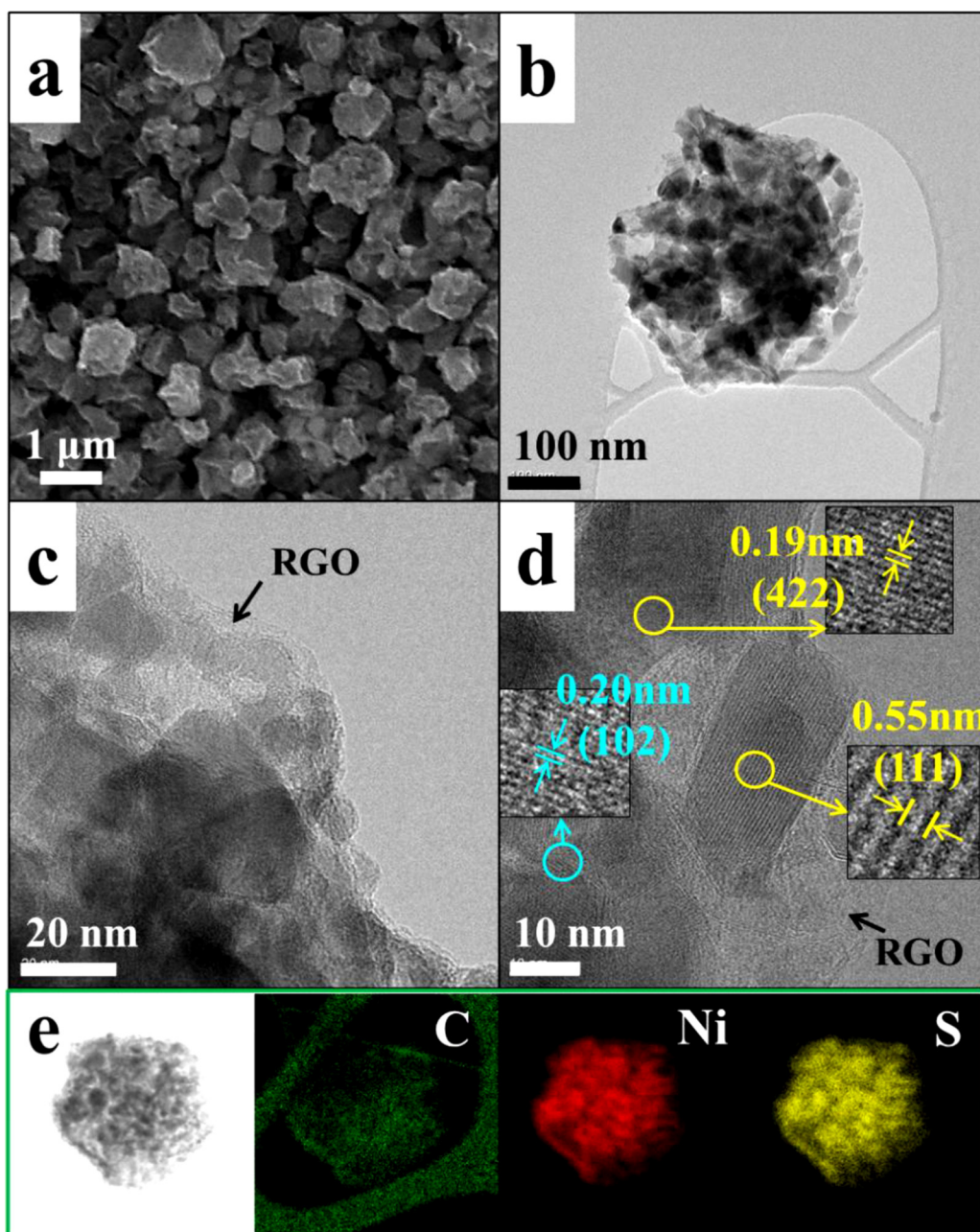
graphene oxide. The concentration of thiourea, which was used as the sulfur source material, affected the crystal structures of the composite powders prepared by spray pyrolysis. The electrochemical properties of the nickel sulfide–RGO composite powders prepared from the spray solution with an optimum amount of thiourea were compared with those of the bare nickel sulfide powders prepared using the same preparation conditions without graphene oxide.

## 2. Experimental section

### 2.1. Synthesis of the bare nickel sulfide and nickel sulfide–RGO composite powders

The bare nickel sulfide and nickel sulfide–RGO composite powders were prepared by one-pot spray pyrolysis from spray

solutions with and without graphene oxide without further heat treatment. Details of the spray pyrolysis process are well described in our previous reports [20,21]. The reactor temperature was maintained at 800 °C to achieve complete sulfidation of the powders, even at a short residence time of the powders inside the hot wall reactor of 8 s. The flow rate of nitrogen used as the carrier gas was fixed at 10 L min<sup>-1</sup>. Graphene oxide (GO) was synthesized from graphite flakes by a modified Hummers method described in our previous report [22]. The as-obtained graphite oxide was re-dispersed in distilled water and then exfoliated to generate graphene oxide sheets by ultrasonication. Nickel nitrate [Ni(NO<sub>3</sub>)<sub>2</sub>] and thiourea [(NH<sub>2</sub>)<sub>2</sub>CS] in various mole ratios were dissolved into 500 mL of an exfoliated graphene oxide dispersion (1 mg mL<sup>-1</sup>) in order to obtain the nickel sulfide–RGO composite powders. The nickel sulfide–RGO composite powders prepared from spray solutions with mole ratios of nickel nitrate to thiourea of 1:2,



**Fig. 1.** Morphologies and elemental mapping images of the NiS–graphene composite powders prepared from the spray solution with Ni nitrate and thiourea in a mole ratio of 1:8: (a) SEM image, (b) and (c) TEM images, (d) HR-TEM image, and (e) elemental mapping images.

Download English Version:

<https://daneshyari.com/en/article/184354>

Download Persian Version:

<https://daneshyari.com/article/184354>

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