

Facile synthesis of cobalt oxide/reduced graphene oxide composites for electrochemical capacitor and sensor applications



Thi Toan Nguyen ^a, Van Hoa Nguyen ^{a, b}, Ranjith Kumar Deivasigamani ^a, Dian Kharismadewi ^a, Yoshio Iwai ^c, Jae-Jin Shim ^{a, *}

^a School of Chemical Engineering, Yeungnam University, Gyeongsan, Gyeongbuk 38541, Republic of Korea

^b Department of Chemistry, Nha Trang University, 2 Nguyen Dinh Chieu, Nha Trang, Vietnam

^c Department of Chemical Engineering, Kyushu University, 744 Motoooka, Nishi-ku, Fukuoka 819-0395, Japan

ARTICLE INFO

Article history:

Received 14 August 2015

Received in revised form

26 October 2015

Accepted 19 January 2016

Available online 20 January 2016

Keywords:

Co₃O₄

Graphene

Nanocomposite

Supercapacitor

Electrochemical sensor

ABSTRACT

Reduced graphene oxide sheets decorated with cobalt oxide nanoparticles (Co₃O₄/rGO) were produced using a hydrothermal method without surfactants. Both the reduction of GO and the formation of Co₃O₄ nanoparticles occurred simultaneously under this condition. At the same current density of 0.5 A g⁻¹, the Co₃O₄/rGO nanocomposites exhibited much a higher specific capacitance (545 F g⁻¹) than that of bare Co₃O₄ (100 F g⁻¹). On the other hand, for the detection of H₂O₂, the peak current of Co₃O₄/rGO was 4 times higher than that of Co₃O₄. Moreover, the resulting composite displayed a low detection limit of 0.62 μM and a high sensitivity of 28,500 μA mM⁻¹cm⁻² for the H₂O₂ sensor. These results suggest that the Co₃O₄/rGO nanocomposite is a promising material for both supercapacitor and non-enzymatic H₂O₂ sensor applications.

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1. Introduction

Transition metal oxides, such as SnO₂, ZnO, MnO₂, Co₃O₄, and Mn₃O₄, have attracted considerable attention for electrochemical capacitor and sensor applications. Among them, Co₃O₄ is a potential candidate for these purposes [1–3] owing to its high theoretical specific capacitance of 3580 F g⁻¹ [4,5], excellent electrochemical redox activity and good reversibility [6]. Co₃O₄, which exhibits catalase – like activity for the decomposition of H₂O₂ [7], can be applied to the detection of H₂O₂ in aqueous medium. On the other hand, the practical applications of supercapacitors and sensors based on Co₃O₄ have been hindered by its relatively poor electrical conductivity [8] and unstable solid electrolyte interface [9]. Moreover, for non-enzymatic sensors, it cannot stand alone for electrode attachment [10].

Several methods have been proposed to improve the electrical conductivity of Co₃O₄-based materials. One of them is to anchor Co₃O₄ onto graphene sheets to form hybrid nanostructures. Graphene has been studied extensively as an ideal matrix for the

growth of metal nanoparticles owing to its high conductivity, electrochemical stability, high surface area, great flexibility, excellent mechanical properties, and rich chemistry [11–13]. Co₃O₄/graphene nanocomposites efficiently enhance the conductivity by a synergetic effect which leads to high electrocatalytic performance [4,8,14].

In this study, Co₃O₄/rGO nanocomposites were synthesized using a facile and environment friendly route. Ammonia was used as the reducing agent instead of toxic, explosive and expensive compounds, such as N₂H₄ [15] or NaBH₄ [16]. Co₃O₄ nanoparticles were coated uniformly over the surface of the rGO sheets without the use of surfactants, such as DDA [14], PVP, CTAB [17], or framework template [18].

2. Experimental

2.1. Materials

Graphite powders (99.9995%), cobalt (II) nitrate hexahydrate (≥98%), ammonium hydroxide (25–28%), hydrogen peroxide (30%), and potassium hydroxide (85%) were purchased from Alfa Aesar, and used without further purification. Deionized (DI) water was used in the entire experimental procedure. Phosphate buffered

* Corresponding author.

E-mail address: jjshim@yu.ac.kr (J.-J. Shim).

solutions (PBS) were prepared from monosodium phosphate and disodium hydrogen phosphate.

2.2. Synthesis of $\text{Co}_3\text{O}_4/\text{rGO}$ nanocomposites

First, GO was synthesized from graphite powder using the improved Hummers method by a 9:1 mixture of concentrated $\text{H}_2\text{SO}_4/\text{H}_3\text{PO}_4$ [19]. GO was then freeze dried at -60°C for 12 h. The $\text{Co}_3\text{O}_4/\text{rGO}$ composite was prepared by mixing 0.01 g of GO and 0.10 g of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in 20.0 ml of DI water, followed by sonication for 30 min. After dropping 0.5 ml of NH_4OH , the light green suspension mixture was transferred to a 40 ml Teflon stain less autoclave, and placed in a laboratory oven for 48 h at 100°C . The black product was collected by centrifugation, washed successively with DI and ethanol then dried in a vacuum oven at 40°C for 6 h. Finally, calcination was carried out at 200°C for 4 h in air to convert all the remaining cobalt hydroxide to Co_3O_4 . Bare Co_3O_4 and rGO were also synthesized using the same method without the addition of GO and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, respectively.

2.3. Characterization

The samples were characterized by X-ray diffraction (XRD; PANalytical, X'Pert-PRO MPD), Fourier transform infrared (FT-IR; Excalibur Series FTS 3000, BioRad) spectroscopy, X-ray photoelectron spectroscopy (XPS; AXIS Nova), thermogravimetric analysis (TGA; SDT Q600, TA instrument), scanning electron microscopy (SEM; Hitachi, S-4200) and transmission electron microscopy (TEM; Philips, CM -200).

Cycle voltammetry (CV), electrochemical impedance spectroscopy (EIS) and other electrochemical measurements were performed using Autolab PGSTAT302N (Metrohm, Netherlands) with a

standard three-electrode cell containing a platinum foil counter electrode, a saturated calomel reference electrode and an active material/glassy carbon (or nickel foam) as the working electrode.

For the sensor test, glassy carbon (GC, $4.5 \times 1.0 \text{ cm} \times \text{cm}$) was cleaned sequentially with acetone and DI water, and dried at 50°C in an oven. In the preparation of $\text{Co}_3\text{O}_4/\text{rGO}/\text{GC}$ or $\text{Co}_3\text{O}_4/\text{GC}$ electrodes, 3 mg of the active material was dispersed in 1 ml ethanol, then dropped onto the surface of GC (1 cm^2). The resulting electrodes were dried at 50°C prior to use.

For the supercapacitor test, the working electrodes were fabricated by mixing the active material (3 mg, 80wt.%) with 15 wt.% acetylene black and 5 wt.% Nafion binder and pressed onto nickel foam current collectors ($1.0 \text{ cm} \times 1.0 \text{ cm}$). The measurements were taken in a 6 M KOH aqueous electrolyte at room temperature. The specific capacitance (C_s) of the electrode was calculated using the following equation: $C_s = It/m\Delta V$, where C_s , I , t , m , and ΔV are the specific capacitance (F g^{-1}), discharging current (A), discharging time (s), mass of active materials (g), and discharging potential range (V), respectively.

3. Result and discussion

3.1. Characterization of composite

The formation of Co_3O_4 was confirmed by XRD, as shown in Fig. 1a. After the calcination process, XRD peaks indexed to the (101) and (102) plane of $\text{Co}(\text{OH})_2$ at 37.72 and 51.36 2θ could not be observed (according the standard JCPDS of $\text{Co}(\text{OH})_2$ no: 003-0913). All the peaks at 18.58° , 30.90° , 36.49° , 38.18° , 44.47° , 55.29° , 59.01° , 64.90° , and 77.13° 2θ were in good agreement with the literature data for Co_3O_4 (JCPDS no. 001-1152). The strong peak of GO corresponding to an interlayer spacing of 0.77 nm at 11.5° 2θ for the

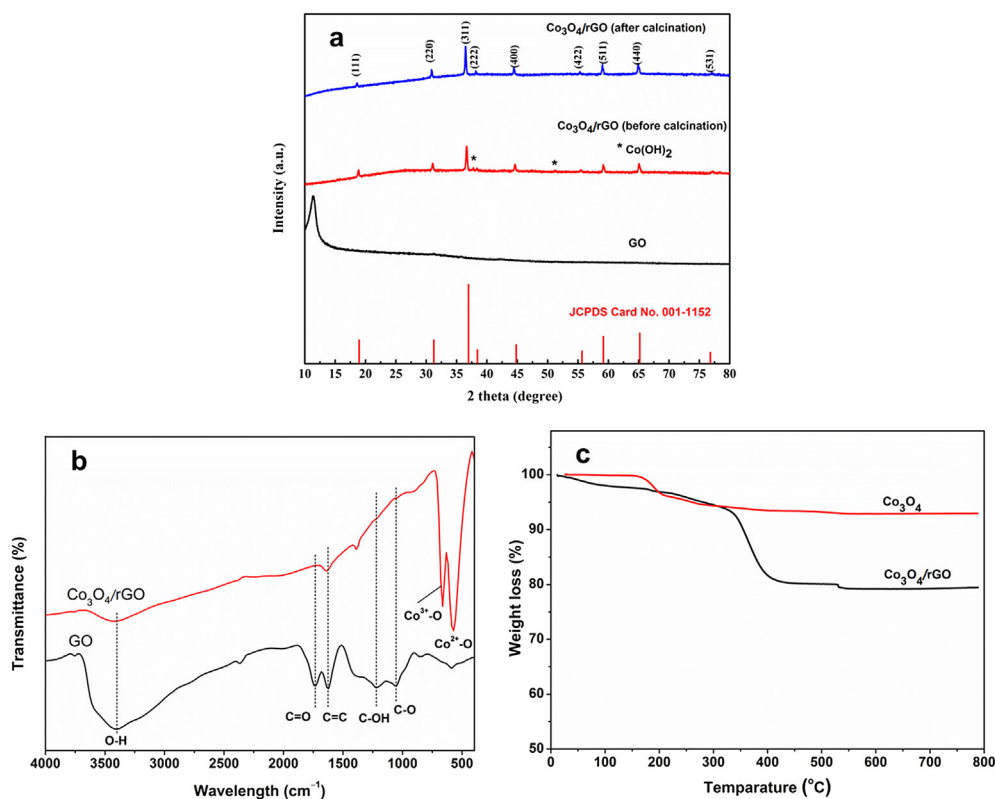


Fig. 1. (a) XRD patterns of GO, $\text{Co}_3\text{O}_4/\text{rGO}$ before and after the calcination process; (b) FTIR spectra of GO and $\text{Co}_3\text{O}_4/\text{rGO}$; (c) TGA curves of Co_3O_4 and $\text{Co}_3\text{O}_4/\text{rGO}$ before calcination.

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