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CoO/rGO composite prepared by a facile direct-flame approach for high-power supercapacitors

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ABSTRACT

In this study, CoO nanoparticles (NPs) measuring approximately 20 nm in size are successfully grown on reduced graphene oxide (rGO) layers through a facile direct-flame approach. The obtained CoO/rGO nanocomposites are applied as electrode materials and show a high specific capacitance, reaching 1615.0 F g^{-1} at a current of 1 A g^{-1} (737.5 F g^{-1} at 50 A g^{-1}), and good cycling stability (88.12% retention after more than 15,000 cycles at 5 A g^{-1}), which are outstanding characteristics compared with those of recently reported pseudosupercapacitors. Furthermore, an asymmetric supercapacitor (ASC) produced using CoO/rGO as a positive electrode material and activated graphene (AG) as a negative electrode achieves a high cell voltage of 1.6 V and delivers a maximum energy density of 62.46 Wh kg^{-1} at a power density of 1600 W kg^{-1}. The fabrication technique is facile and represents a promising means of obtaining metal oxide/graphene composites for high-performance supercapacitors.

1. Introduction

Supercapacitors have attracted considerable interest due to their rapid charge-discharge rate, long cycle life, and superior power density [1–4]. In recent years, studies in the field of supercapacitors have focused on employing hybrid materials to improve the energy density of supercapacitors. Among the various types of electrode materials, transition metal compounds exhibit a longer cycling stability than conductive polymers and a higher specific capacitance than carbon-based materials [5–9]. These compounds feature a low material cost, high compatibility with neutral electrolytes, and environmental friendliness [10]. Cobalt oxides, which are a good example of these compounds, have attracted extensive interest [11–15], and thus are often applied in the production of supercapacitor electrode systems [16–20].

An ideal supercapacitor electrode material generally has a large ion-accessible surface area, high electrical conductivity, high ionic transport rate and good electrochemical stability. An effective way to achieve these aims is to rationally explore and design novel-structured electrode materials with high specific capacitance [21–24]. In this regard, graphene-based composites, such as metal oxide/graphene [25,26], metal hydroxide/graphene [27,28] and polymer/graphene [29–31], have been demonstrated as promising supercapacitor electrode materials. However, driven by the strong π–π interaction, graphene sheets readily re-stack in a parallel manner to form graphite-like powders during processing, leading to a severe reduction in the specific surface area, which presents a serious obstacle to the use of graphene. A wide variety of methods, including thermal annealing [32], micromechanical cleavage [33], chemical vapor deposition [34,35], epitaxial growth [36], and chemical exfoliation [37,38], have been developed to manufacture graphene sheets. However, the existing methods often require high temperatures, an inert gas atmosphere, and time-consuming gas reduction treatment. Thus, the development of a highly efficient and simple alternative method to restore the p-conjugated structure of graphene oxide (GO) is very intriguing and worthy of further exploration.

It is well-known that a flame can work as a fuel reformer for the production of synthesis gas (H_2 and CO) via partial oxidation. Notably, a flame can remotely induce the local reduction of GO and can significantly enlarge the specific surface area within a few seconds in air. Chen and coworkers successfully reduced GO by burning GO powder swelled in three types of flames, namely, those fueled by acetone, methanol and ethanol, under the flame atmosphere [39]. Later, Yan et al. reported that reduced graphene oxide (rGO) paper was easily synthesized by flame-induced reduction of GO paper under ambient conditions. The flame-induced reduction significantly increased the rGO surface area, and an appropriate content of groups oxygen-containing groups was retained on the graphene sheets [40]. Yang et al. exposed a graphene oxide/Ni foam composite to an epitaxial flame for a

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few seconds and obtained rGO/Ni foam; a three-dimensional hierarchical porous structure with numerous oxygen-containing groups was obtained [41].

Based on these studies and our previous work [42], we designed an efficient and simple route to synthesize a CoO/rGO composite for potential application as a supercapacitor electrode as follows: (1) A 2D-GO sample was used as a template for Co to direct deposition and heterogeneous nucleation. (2) The size of the nanoparticles (NPs) was tailored by carefully controlling the pH (3) The direct-flame approach was employed for formation of CoO and to convert the GO into rGO. It would be desirable to combine the advantages of graphene, i.e., large surface area, chemical stability and high electrical conductivity, with those of cobalt oxide, i.e., its pseudocapacitive behavior and enhanced energy storage. To the best of our knowledge, the proposed synthesis method has never been explored for cobalt oxides. As a binder-free electrode for capacitors, the optimized CoO/rGO composite shows a high specific capacitance of up to 737.5 F g^{-1} at a current of 50 A g^{-1} and high cycling stability, demonstrating excellent electrochemical performance. Furthermore, an asymmetric supercapacitor (ASC) was designed using CoO/rGO as the positive electrode, activated graphene (AG) as the negative electrode, and 2 M KOH as the electrolyte. The ASC can achieve a high cell voltage of 1.6 V and can deliver a maximum energy density of 62.46 Wh kg^{-1} at a power density of 1600 W kg^{-1}. This flame-induced fabrication technique is simple and eco-friendly, making it a promising approach for producing metal oxide/graphene for supercapacitors.

2. Experimental

2.1. Materials and chemicals

Graphite powder (99.99%) was purchased from the Qingdao Jinrilai Graphene Corporation. Sodium nitrate ($NaNO_3$, ≥98.0%), ethanol (CH_3CH_2OH, ≥98.0%), and hydrogen peroxide (H_2O_2, 30.0%) were obtained from the Chengdu Kelong Reagent Factory. Potassium permanganate ($KMnO_4$, 99.0%), ammonium hydroxide solution (NH_4OH, AR), and sulfuric acid (H_2SO_4, 98.0%) were purchased from Chongqing Chuandong Chemical (group) Co., LTD. Cobalt (II) acetate tetrahydrate ($C_4H_{14}CoO_8$, > 99.0%) was purchased from GENERAL-REAGENT. All reagents were of analytical-reagent grade and were used without further purification. Deionized (D.I.) water was used throughout the experiments.

2.2. Preparation of the CoO/rGO composite

2.2.1. Synthesis of graphene oxide (GO)

GO was prepared through a modified Hummer's method from graphite powder following a previous report (see the Electronic Supporting information (ESI†) for details).

2.2.2. Synthesis of $Co(OH)_2$/GO film

Briefly, 400 mg of GO was added to 100 mL of distilled (DI) water, and this mixture was ultrasonicated for 1 h to form a suspension. The suspension was then transferred to a three-necked round-bottom flask and stirred at 25 °C in a water bath. $Co(Ac)_2$ (0.02 M, 100 mL) solution was dropped into the above suspension, followed by the addition of ammonia solution ($NH_3{\cdot}H_2O$, 20 wt%), which was then stirred for a few hours to guarantee a complete reaction. The obtained $Co(OH)_2$/GO composite precursor was dried at 50 °C under vacuum. Finally, we obtained a $Co(OH)_2$/GO hybrid film.

2.2.3. Synthesis of CoO/rGO

The hybrid film was quickly passed through the naked flame of a burning alcohol lamp (video, see the ESI†). The color of the $Co(OH)_2$/GO film changed from yellow-brown to black, and CoO/rGO was obtained.

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2.3. Electrode preparation

First, to construct a three-electrode system, the as-prepared CoO/rGO samples were ground into a fine powder and directly pressed between two nickel foam pieces (1 × 1 cm^2) to form the working electrode in the three-electrode system. The mass loading of CoO/rGO was approximately 2–2.5 mg.

Next, a two-electrode system was prepared. The CoO/rGO samples were pressed between two nickel foam pieces (1 × 1 cm^2) to form the positive electrode, and the AG (see the ESI† for details) was pressed between two other nickel foam pieces to form the negative electrode.

2.4. Material characterization

Raman measurements were collected with a Raman spectrometer (LabRam HR Evolution, Horiba). X-ray diffraction (XRD) patterns were determined by an X-ray diffractometer (SuperNova, Agilent), and X-ray photoelectron spectrum (XPS) measurements were acquired using an X-ray photoelectron spectrometer (L Escalab 250Xi, Thermo Fisher Scientific). FE-SEM images were obtained on a JEOLJSM-7800F microscope, and TEM images were taken on Tecnai G2 20 microscopes. BET measurements were obtained with a BET surface area analyzer and a pore size analyzer (Beishide 3H-2000PS1). In addition, the electrical conductivity was tested using a 4-point probe resistivity measurement system (PROBES TECH RTS-9).

2.5. Electrochemical measurements

In the three-electrode system, which includes a working electrode, a platinum plate, and a saturated calomel electrode (SCE), electrochemical tests were performed at a temperature of 25 °C. All of the electrochemical measurements were carried out in 2 M KOH solution via a CHI-760E electrochemical workstation. Cyclic voltammetry (CV) analysis was performed for a potential window range from 0 to 0.5 V at 1, 2, 5, 10, 20, 30, and 50 mV s^{-1}. Galvanostatic charge-discharge (GCD) tests were carried out for a potential window of 0–0.4 V at 1, 2, 5, 10, 20 and 50 A g^{-1}. Electrochemical impedance spectroscopy (EIS) measurements were recorded in the frequency range from 0.01 to 100 kHz at a 5-mV AC voltage.

To further investigate the capacitive ability of the CoO/rGO electrode for real applications, a two-electrode system using 2 M KOH as an electrolyte was fabricated. The positive and negative electrodes were prepared as described in Section 2.3.

3. Results and discussion

3.1. Material characterization

Fig. 1a presents a typical XRD pattern of the as-prepared CoO/rGO composite. The relatively weak (111), (200), and (220) diffraction peaks can be ascribed to the well-crystallized CoO and are assigned to the standard cubic structure of CoO (JCPDS no. 43-1004) [43]. Compared with pure CoO, the CoO/rGO composite shows an additional small and narrow (002) diffraction peak appearing at a 2θ of 24.5°∼27.5° [44], which may be due to the disordered stacked graphene sheets.

The Raman spectra (Fig. 1b) exhibit typical characteristic peaks for the D-band (vibration of carbon atoms with dangling bonds) and G-band (vibration of all sp^2-bonded carbon atoms) of carbon at approximately 1605 and 1357 cm^{-1}, respectively. Notably, the two sharp peaks at 501 and 658 cm^{-1} appearing in the spectrum of CoO/rGO are attributed to the $F2_g$ mode and $A1_g$ mode of CoO, respectively.

To determine the detailed chemical composition of the CoO/rGO composite, XPS tests were performed from 0 to 1200 eV (Fig. 2a). From