



Insight into graphene/hydroxide compositing mechanism for remarkably enhanced capacity



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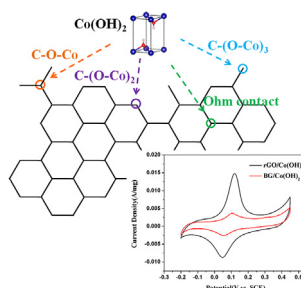
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HIGHLIGHTS

- CH₂ groups transform into Co-O-C bonds as the bridge between graphene and Co(OH)₂.
- rGO/Co(OH)₂ exhibits a highly crystalline feature.
- BG/Co(OH)₂ holds more Co³⁺ ions and Co-O tetrahedral structures.
- C-(O-Co)_n affords abundant electron transport channels.
- A dramatically high specific capacity of 1368 F/g is achieved for rGO/Co(OH)₂.

GRAPHICAL ABSTRACT



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ABSTRACT

The interaction between active materials and conductive additives is complicated but crucial within electrochemical energy storage devices. Here, we first identify that CH₂ groups drive the compositing process, leading to an effective formation of Co-O-C chemical bonding serving as the bridge between reduced graphene oxide (rGO) and hydroxide. Due to the enhanced electron transport, a dramatically improved specific capacity is achieved as high as 1368 F/g for rGO/Co(OH)₂ electrode at a current density of 0.5 A/g. Thus, we provide new insights into graphene/hydroxide compositing mechanism, which has a significant impact on enhancing electron transport for a variety of graphene/hydroxide in energy storage systems.

1. Introduction

To meet the ever-growing demand of energy, transition metal

compounds (TMCs, including but not limited to oxides, hydroxides and sulphides) have been widely studied as electrodes in energy storage devices, with merits such as high electrochemical activity, high current

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density and short charging time [1–4]. The poor conductivity of TMCs leads to low redox activity and insufficient reaction [5]. It is an effective way to composite TMC with conductive additives [6]. However, the connection between active materials and additives determines the overall electron transport process, and thus the final performance. So, insights into the compositing mechanism between TMC and the additives are necessarily needed.

Graphene is an attractive two-dimensional material with high surface area and electrical conductivity [7–9]. Many reports on the composites of graphene and TMCs have achieved promoted performances [10–15]. The interaction between TMC and graphene essentially affects the electron transport and capacitive performance [10,12,13,15–19]. To date, many studies have been carried out on such interaction mechanism as it exists in abundant crystalline/amorphous phases [20,21], and accounts for variant valence state [22], defects [12], irregular morphologies [23–27] and synergistic effect [14,28]. The complexity of interactions can also be increased through redox reactions of various species [29–31], diverse nucleation/growth scenarios [17,32] and electron transport [15,33]. But still two fundamental questions remain: What is the connection between active materials and graphene? How interactions between graphene and TMC affect electron transport and redox activity? To address these critical issues for enhanced performance, the composite material should be delicately designed.

Herein, we synthesized layered cobalt hydroxide (Co(OH)_2) nanosheets composited with reduced graphene oxide (rGO/Co(OH)_2) and B_xO_y modified graphene (BG/Co(OH)_2) as active material to explore the interaction between Co(OH)_2 and graphene. B_xO_y was chosen to alter the surface state and functional groups of graphene, and it will further affect the connection between Co(OH)_2 and graphene. Thus the different electrochemical behaviours can show us the insights of the interaction and its influence. As a result, it tends to grow amorphous small Co(OH)_2 nanosheets in BG/Co(OH)_2 , which may reduce the Co–O–C bonding, hindering the electron transport and leading to a poor capacitive behaviour. However, rGO/Co(OH)_2 can afford good crystallization in integrated hexagonal Co(OH)_2 nanosheets, forming abundant Co–O–C bonding via CH_2 group. Co–O–C bonding as the bridge between graphene and Co(OH)_2 can accelerate electron transport and promote redox activity of Co(OH)_2 . The synthesized rGO/Co(OH)_2 exhibited a high capacity of 1368 F/g, which was dramatically superior compared with BG/Co(OH)_2 (556 F/g). Rather than the effect of the delicate control on crystallinity and morphology of Co(OH)_2 nanosheets, such excellence is attributed to the interaction between graphene and Co(OH)_2 , resulting in promoted electron transport and enhanced capacity. This work will pave new ways to improve electrochemical performance for a variety of similar systems.

2. Experimental section

2.1. Preparation of rGO and BG

Graphene oxide (GO) was prepared by Hummer methods from natural graphite [34]. Further, the GO samples were cooled at -65°C for 5 h and vacuum drying for 32 h in a freeze drying process. The rGO samples were prepared by heating as-prepared GO samples to 1000°C in a tube furnace at a He/H_2 atmosphere with the following temperature ramps: in $20^\circ\text{C}/\text{min}$ to 600°C , then $10^\circ\text{C}/\text{min}$ to 900°C , finally $5^\circ\text{C}/\text{min}$ to 1000°C , and held in thermal insulation for 1 h followed by natural cooling. The BG samples were prepared by placing 200 mg of GO into 60 mL deionised water and ultrasonicing for 5 min. Then, 0.025 mol B_2O_3 (Sinopharm Chemical Reagent Co., Ltd, > 98.0%) was placed into 10 mL 90°C hot deionised water and ultrasonic for 5 min. The resulting GO and B_2O_3 solutions were mixed and ultrasonic for 5 min. After a freeze drying process, the mixture placed in a tube furnace was heated. The freeze drying process and heating conditions were set the same as the preparation of rGO samples. Further, the samples were washed with 90°C hot deionised water and dried in a 100°C oven

for 12 h. Finally, the samples were collected by suction filtration twice and placed in a blast air oven at 100°C for 12 h [35]. Fig. S1(a) shows a schematic representation of the preparation of rGO, BG, rGO/Co(OH)_2 and BG/Co(OH)_2 . EDX and XPS in Fig. S2 demonstrated the existence of B element, demonstrating that B_2O_3 was successfully incorporated into graphene.

2.2. Preparation rGO/Co(OH)₂ and BG/Co(OH)₂ samples

A typical route for synthesis of rGO/Co(OH)_2 and BG/Co(OH)_2 was used with a weight ratio of 30 wt% for Co(OH)_2 . The specific route is as follows: 0.771 g $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$ (Sinopharm Chemical Reagent Co., Ltd, $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$, > 99.0%) and 0.504 g hexamethylenetetramine (HMT) were dissolved in a 60 mL mixture of water and ethanol with the volume ratio of 9:1 and stirred for 1 h. Then, the prepared rGO or BG was added to the mixture. After ultrasonicing for 15 min, the mixture was poured into a round bottomed flask and heated to 90°C in an oil bath with stirring for 1 h. The solution then became pink with black particles. The black particles were then filtrated, washed, and finally dried in air at 60°C overnight. The obtained powers from suction filtration were defined as rGO/Co(OH)_2 or BG/Co(OH)_2 and dried for further characterization.

2.3. Materials characterization

Power X-ray diffraction (XRD) analysis was performed on a Bruker D8 Advance diffract meter with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ nm}$). Raman spectra were carried out by a Raman microscope (T64000 (Horiba) with a 514.5 nm Ar^+ laser excitation). Fourier transform infrared spectroscopy (FTIR) spectra of KBr powder pressed pellets were obtained from Perkin Elmer Spectrum One B instrument. Morphologies of the as-obtained samples were analysed by using a scanning electron microscope (SEM, Hitachi SU8010) and transmission electron microscope (TEM, JEM-2100F).

The Co–K-edge XAFS spectra were measured on the 1W2B & 4W9B baseline at room temperature in Beijing Synchrotron Radiation Facility (BSRF). The data was analysed and fitted using Athena and Artemis software. The surface electronic states were identified by X-ray photoelectron spectroscopy (XPS) (ESCALAB-250 performed with a monochromatic $\text{Al K}\alpha$ radiation source and a hemisphere detector with an energy resolution of 0.1 eV.

2.4. Electrochemical characterization of the electrodes and asymmetric supercapacitors(ASC)

Electrochemical characterization of the electrodes was conducted in a typical three-electrode system, in which clean platinum foil and saturated calomel electrode (SCE) were used as the counter electrode and reference electrode. The ASC was assembled in a CR2032 battery coin with rGO/Co(OH)_2 on carbon nanofiber (CNF) as positive electrode, AC on CNF as negative electrode, and 1 M KOH solution as electrolyte. The mass of Co(OH)_2 and AC was 0.374 and 2.53 mg, respectively. The diameter of the electrode plate was measured as 16.19 mm (Fig. S3). The ASC was carried out in a two-electrode system. Cyclic voltammogram (CV) and galvanostatic charge-discharge (GCD) tests were conducted using a CHI660E electrochemical workstation (Shanghai CH Instrument Company, China). The electrochemical impedance spectroscopy (EIS) of the electrodes was conducted on a PARSTAT 2273 advanced electrochemical system (American). The working electrode was prepared by mixing 85 wt% of rGO/Co(OH)_2 or BG/Co(OH)_2 , 10 wt% of conducting graphite (Alpha Aesar, conducting grade, -325 mesh, 99.9995%), and 5 wt% Nafion solution (DuPont). The mixture was then pressed onto CNF and dried at 60°C in vacuum above 12 h.

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