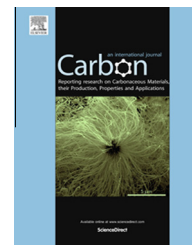


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# High-capacity graphene oxide/graphite/carbon nanotube composites for use in Li-ion battery anodes

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## ABSTRACT

A composite of graphene oxide sheets, carbon nanotubes (CNTs), and commercial graphite particles was prepared. The composite's use as a high-capacity and binder-free anode material for Li-ion batteries was examined. Results showed that this novel composite had a very high reversible Li-storage capacity of 1172.5 mA h g<sup>-1</sup> at 0.5C (1C = 372 mA g<sup>-1</sup>), which is thrice that of commercial graphite anode. The composite also exceeded the theoretical sum of capacities of the three ingredients. More importantly, its reversible capacity below 0.25 V can reach up to 600 mA h g<sup>-1</sup>. In summary, the graphene oxide/graphite/CNT composite had higher reversible capacity, better cycling performance, and similar rate capability compared with the graphene oxide/graphite composite.

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## 1. Introduction

Rechargeable Li-ion batteries (LIBs) are widely used in portable electronic devices and electric vehicles. Electrode materials are the key components responsible for the electrochemical properties of LIBs. Currently, the anode material of commercial LIBs is based on graphite because of the latter's excellent stability [1], safety [2], and affordability. However, graphite has a maximum theoretical Li-storage capacity of only 372 mA h g<sup>-1</sup> [3], which hardly satisfies the changing requirements of portable electronic devices and recently developed fully electric vehicles. To improve the capacity, life cycle, and rate capability of LIBs, a considerable number of studies has focused on advanced carbonaceous materials, including mesoporous carbon micro beads (MCMB) [4], hard carbon materials [5], carbon nanofibers [6], carbon nanotubes

(CNTs) [7], and graphene [8]. However, reports on the direct use of graphene oxide as anode material in LIBs are limited.

In our previous work, we have shown that graphene oxide can be directly used in LIBs [9]. As a possible anode material, graphene oxide demonstrates an excellent performance, with a high capacity of 704.7 mA h g<sup>-1</sup> at a current rate of 0.5C (1C = 372 mA g<sup>-1</sup>). However, graphene oxide is unstable when subjected to electrochemical cycling after its compositing with commercial graphite. In the present study, we added CNTs to the above composite in an attempt to enhance its capacity, with the consideration that CNTs often used as conductive additives [10] possess a special one-dimensional (1D) structure, high electrical conductivity, and good transfer channels.

By compositing graphene oxide, graphite, and CNTs with the conductive additive (denoted as GGCC), a binder-free anode material with a high specific capacity was successfully

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synthesized. Compared with commercial anode materials that require polymeric binders and negatively affect the cost, specific capacity, and conductivity of LIBs [1], our GGCC composite can be directly used as an electrode without a need for any other binder. As such, our composite presents a solution to the abovementioned problems. Furthermore, graphite particles and CNTs were homogeneously distributed throughout graphene oxide sheets, which effectively prevented the restacking of the said sheets and promoted the easier movement of electrons within the electrode. Results of electrochemical tests indicated that the novel GGCC composite had very high reversible capacity, excellent rate capability, and cycling stability.

## 2. Experimental

### 2.1. Synthesis of materials

All chemical reagents used to prepare graphene oxide were analytical grade (purchased from Chengdu Kelong Chemicals Co., Ltd.) and used as received. Graphene oxide was synthesized from high-purity natural graphite flakes (about 200 meshes, 99.999% purity; Changsha Shenghua Research Institute) using the Hummers method [11]. In a typical synthesis, 5 g of natural graphite flakes was added to 115 ml of  $\text{H}_2\text{SO}_4$  (98%) with vigorous stirring in an ice bath. Then, 15 g  $\text{KMnO}_4$  was slowly added to the reaction vessel five times. Afterwards, 230 ml of deionized water and 30 ml of  $\text{H}_2\text{O}_2$  were added to the suspension. The ice bath was removed and then subjected to centrifugal separation and repeated washing using dilute hydrochloric acid and deionized water. The colloidal dispersion of the as-synthesized graphene oxide in deionized water at a concentration of  $1 \text{ mg ml}^{-1}$  was prepared with the aid of ultrasonication (20 kHz ultrasound probe) for about 15 min until stabilization and browning of the dispersion.

The CNTs used in the GGCC composite were multi-walled CNTs purchased from Chengdu Organic Chemicals Co., Ltd. (CAS). The conductive additive used in the GGCC composite was Super-P carbon black (SP; 40 nm,  $62 \text{ m}^2 \text{ g}^{-1}$ ), purchased from TIMCAL Graphite & Carbon Co. The commercial graphite (characterized in Fig. 1a) used in the GGCC composite was purchased from BTR New Energy Materials Inc., Shenzhen (diameter, 8–15  $\mu\text{m}$ ; pellet density, 1.45–1.60  $\text{g cm}^{-3}$ ). For electrochemical tests, anode slurries were prepared by mixing adequate deionized water with the GGCC composite. The battery performances of the composites highly depended on the graphene oxide/graphite/CNT weight ratios. The highest capacities were obtained in from the composite with graphene oxide, graphite, CNT, and SP mass ratios of 15:60:20:5. The slurry was prepared by mixing adequate deionized water with the GGCC composite under vigorous stirring for 3 h. The resultant slurry was uniformly pasted onto a Cu foil with a blade. The prepared electrode sheets were dried at 120 °C in a vacuum oven for 12 h and subjected to a pressure of approximately  $200 \text{ kg cm}^{-2}$ . The electrodes of graphene oxide, graphite, and CNTs were prepared using the same processes with (a) graphene oxide and SP at a weight ratio of 85:15; (b) graphite, carboxymethyl cellulose (CMC; MW, 90,000; Aldrich), and SP at a weight ratio of 85:10:5; and (c) CNTs, CMC, and SP at a weight ratio of 85:10:5.

### 2.2. Characterization

The morphology and structure of the obtained samples were determined by scanning electron microscopy (SEM; INCA PentafETx3) with energy-dispersive X-ray spectrometry (EDS) and transmission electron microscopy (TEM; JEM-100CX JEOL). X-ray photoelectron spectroscopy (XPS; PHI5600 Physical Electronics) was performed using  $\text{Al/K}\alpha$  radiation ( $h\nu = 1486.6 \text{ eV}$ ) to determine elemental compositions and assignments of carbon peaks. X-ray diffraction (XRD) patterns were obtained from X'Pert MPD DX2700 using  $\text{Cu/K}\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ). Nitrogen adsorption–desorption isotherms at  $-196 \text{ }^\circ\text{C}$  were obtained using a Builder SSA4200 apparatus. Specific surface areas and porosities were calculated using the Brunauer–Emmett–Teller and Barrett–Joyner–Halenda methods based on the adsorption branches of the isotherms (Supplementary materials Fig. S1).

### 2.3. Electrochemical measurements

Electrochemical measurements were conducted using two-electrode CR2032 coin cells assembled in an argon-filled glove box. The electrolyte, obtained from Capchem Technology (Shenzhen) Co., Ltd., consisted of a solution of 1 M  $\text{LiPF}_6$  in ethylene carbonate, dimethyl carbonate, diethyl carbonate (1:1:1, v/v). The separator used in the battery was Celgard 2400. A Li foil was used as the counter and reference electrode. Galvanostatic charge and discharge experiments were conducted at various rates on a BS-9300R battery test system within the potential range of 0.01–3.0 V versus  $\text{Li}^+/\text{Li}$ . Electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) tests were performed on a PARSTAT 2273 workstation.

## 3. Results and discussion

### 3.1. Characterization of materials

Fig. 1a and b present the micro-appearance of commercial graphite particles and multi-walled CNTs with an outer diameter of about 20–50 nm. Fig. 1c and d show the SEM and TEM images of the as-synthesized two-dimensional paper-like graphene oxide sheets. Fig. 1c shows that the oven-dried graphene oxide sheets easily form a soluble aggregate. After ultrasonication in deionized water (Fig. 1d), a nearly single layer of graphene oxide sheet is obtained from the aggregate. Corrugation and scrolling are part of the intrinsic nature of graphene oxide sheets. As such, nanovoids and nanocavities are to be expected in the GGCC composite. Fig. 1e shows that the rough surface of commercial graphite becomes smooth after compositing, indicating that it is uniformly wrapped by graphene oxide sheets. Moreover, at the junction of two graphite particles, the CNTs partly or fully wrapped by graphene oxide sheets make a bridge and form a conductive network. This structure helps enhance electron transfer between graphite particles and between graphene oxide sheets. More importantly, no obvious agglomeration is observed. Graphene oxide maintains its typical wrinkled paper-like structure after compositing with graphite and CNTs. The TEM image shown in Fig. 1f confirms this effect of the GGCC composite. Graphene oxide sheets cover the

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