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Graphene-winged carbon nanotubes as high-performance lithium-ion batteries anode with super-long cycle life

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HIGHLIGHTS

- G-CNTs are fabricated by the well-controlled outer-wall peeling of MWCNTs.
- G-CNTs can self-assemble into 3D loose strip-type structure with the curly edges.
- The edge- and defect-rich GNS enhanced the electrochemical performance of LIBs.
- G-CNTs anode delivers reversible capacity as high as 603 mAh g^{-1} over 2200 cycles.

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ABSTRACT

Graphene-winged carbon nanotubes (G-CNTs) have been prepared by the well-controlled outer-wall peeling of the multi-walled carbon nanotubes (MWCNTs). The final hybrid structure features the few layers of graphene nanosheets attaching to the intact inner walls of CNTs. On one hand, the outer branched graphene nanosheets could suppress the aggregation of CNTs and introduce abundant defects and active-edges for easily accessible chemical interaction. On the other hand, the CNTs could bridge the graphene nanosheets for rapid electron transfer and mechanical robustness. As a result, the G-CNTs was used as the electrode materials exhibiting an extremely steady reversible capacity of 603 mAh g^{-1} over 2200 cycles at a current density of 1 A g^{-1} (the corresponding area capacity is 0.16 mAh cm^{-2} at a current density of 0.26 mA cm^{-2}) and owning a high rate capability much superior to those of the pristine MWCNT-based counterparts. The hierarchical G-CNTs architecture provides a new material platform for development of advanced energy-storage devices.

1. Introduction

Rechargeable lithium-ion batteries (LIBs) have triggered tremendous attention owing to their environmental friendliness, high energy density and long lifetime, and provided suitable levels of power for many applications and requirements of daily life. In terms of the high-performance LIBs, the electrode materials play an important role in dominating their electrochemical properties. However, graphite, the commercial anode material for LIBs, can hardly fulfill the increasing requirements of various consumer electronic devices because of its low theoretical capacity of around 372 mAh g^{-1} (exhibiting an intercalation reaction with lithium to yield LiC_6) and limited rate capability [1,2]. To pursue an excellent performance of LIBs, the anode materials possessing such characteristics as large specific surface areas with abundant active sites, high electrical conductivity and stable multi-stacking with short diffusion lengths are highly desirable [3]. In this regard, nanostructured carbonaceous materials, including the multi-walled carbon nanotubes (MWCNTs) and graphene, can meet the above-mentioned demands for high power density materials and have been regarded as the most promising candidates for the traditional graphite anode.

MWCNTs, rolled up by multilayer graphene, have attracted immense interests from the researchers owing to their fascinating properties such as high aspect ratio (ratio of length to diameter which is > 10,000), superior mechanical properties (with a Young's modulus and tensile strength of 1.2 TPa and 50–200 GPa, respectively) and excellent electrical conductivity (>10^5 S m^{-1}) [4–6]. Recently, detailed investigations based on the density functional

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theory reveal that lithium ion (Li^+) can quickly penetrate into the graphene layers of MWCNTs and the interstitial spaces between neighboring ones [7,8], leading to an enhanced capacity than that of graphite. However, MWCNTs easily self-aggregate to form congeries with many boundaries because of their high surface energy and van der Waals force [9], which are not favorable for Li^+ diffusion and electron transport, while significantly reducing the contact surface between the electrolyte and MWCNTs. What is worse, since the raw MWCNTs are end-closed, Li^+ can be only localized at the outside surface of MWCNTs if no extra treatments were employed, resulting in the reduction of active sites. Therefore, the advantage of MWCNTs compared to graphite is limited and unsatisfactory so far for battery applications. Despite some attempts about tailoring or modifying the pristine MWCNTs have been made to improve their electrochemical properties, such as acid oxidation [10,11], ball milling [12], cutting [13], drilling holes [14], opening cap [15] and so on, it is still a challenging task for MWCNTs to make real breakthroughs to obtain the high-performance LIBs.

Graphene, a two-dimensional (2D) monolayer of sp^2-hybrized carbon atoms, is an ideal electrode material for LIBs with high electrical conductivity, large theoretical specific surface area (2630 $m^2\ g^{-1}$) and good chemical stability, which can be used as an electrically conductive channel to fast electron transfer [16]. Unfortunately, although graphene nanosheets possess additional advantages, they also easily stack and condense together because of their high surface energy and strong interlayer van der Waals interactions [17]. In our previously reported paper, a porous and ultralight 3D graphene framework was readily prepared by a one-step hydrothermal method followed by calcination based on graphene oxide as the precursor [18]. The experimental evidence suggested that the 3D graphene foam only had a specific surface area of approximately 280 $m^2\ g^{-1}$, which was *ca.* 9.4 times lower than the theoretical value. Restricted to the layer-by-layer self-stack, the graphene anode had a low contact area with electrolyte, a poor-rate capability and cycling stability. In addition, the graphene typically suffered mechanical degradation during the long-term cycling, which can be attributed to repetitive lithiation/delithiation-induced agglomeration and detachment from the conducting environment [19], thus further leading to a larger degree of packing.

To conquer these drawbacks of the individual CNTs or graphene as anode materials for LIBs, the effective bonding CNTs and graphene to form three-dimensional (3D) hierarchical composites is a better approach to enhance the overall performance. Up to now, it's still a bottle-neck for facile integration of high-quality CNTs/graphene hybrids without barrier layers, though several strategies have been explored, including the simply physical mixing [20], direct chemical vapor deposition growth through growing CNTs on graphene layers [21], in-situ growth of graphene/CNTs hybrids on Cu foil coated with an Fe catalyst layer [22], and so on. However, the proposed synthesis is generally more challenging for commercial application due to the difficulty of large-scale fabrication, the need of special equipment, high temperature and the complicated process. Among these methods, one of the major drawbacks is the need of multi-functional catalysts to grow CNTs and a uniform substrate for the deposition of graphene layers, which easily introduces some non-carbon impurities and constrains the intrinsic feature of graphene and CNTs.

Herein, the graphene-winged CNTs (G-CNTs) have been prepared by a well-controlled outer-wall peeling process of the MWCNTs, which are composed of outer edge-rich graphene nanosheets and inner intact CNTs (also donated as GNS@CNT). Distinguished from previously reported CNTs-on-graphene architecture [21–23], the GNS@CNT possesses the bridged-structure that the outer peeled graphene nanosheets attached to the inner intact walls of CNTs. The homogeneously linked graphene nanosheets would act as the basic connecting point to assemble the partially unraveling CNTs side-by-side to suppress the aggregation of CNTs, meanwhile the introducing abundant defects and heteroatom (e.g., oxygen) to increase additional active sites for Li^+ storage. On the other hand, the inner CNTs can serve as conductive bridges to connect adjacent graphene sheets and provide the highly electrically conductive pathway. Benefiting from the advanced properties of bridged-structure, the GNS@CNTs can self-assemble into 3D loosed strip-type architecture by freeze-drying, which can shorten Li^+ diffusion lengths and provide more active sites for Li^+ storage. Finally, the lyophilized sample was annealed at 500 °C and subsequently employed to the assembly of the cell. As the anode material for LIBs, the G-CNTs electrode exhibits an extremely steady reversible capacity of 603 $mAh\ g^{-1}$ over 2200 cycles at a current density of 1 $A\ g^{-1}$ (the corresponding area capacity of the electrode is 0.16 $mAh\ cm^{-2}$ at a current density of 0.26 $mA\ cm^{-2}$) and owns a high rate capability (210 $mAh\ g^{-1}$ at 5 $A\ g^{-1}$, <3 min to fully charge).

2. Experimental section

2.1. Synthesis of ox-GNS@CNT

The ox-GNS@CNT was successfully synthesized *via* the longitudinal and partial peeling of MWCNTs using a chemical oxidation method [24–26]. Briefly, 0.2 g of the pristine MWCNTs (purchased from Nanjing pioneer nanometer company, China) were mixed with 50 mL concentrated sulphuric acid (H_2SO_4) in a glass container and stirred for 30 min in ice-water bath. After that, 5.6 mL phosphoric acid (H_3PO_4) and 0.8 g potassium permanganate ($KMnO_4$) was slowly added into the mixture and kept stirring for another 30 min. Then, the reaction mixture was heated at 70 °C for 2 h. After cooling to room temperature, the mixture was poured into 80 mL of ice-water containing hydrogen peroxide (H_2O_2) (30%, 2 mL). Subsequently, the inorganic acid was removed by centrifugation directly and then washed by 5 wt % HCl solution to get rid of the impurities. Finally, the product was thoroughly purified by dialysis using deionized water for several days until neutral condition. The final field is about 0.18 g.

For comparison, ox-GNR (completely peeled MWCNTs) was also prepared under experimental conditions identical to those used in the synthesis of ox-GNS@CNT except adding 1.0 g $KMnO_4$ and prolonging the oxidized time to 4 h at the temperature of 70 °C.

2.2. Synthesis of 3D-GNS@CNT

The ox-GNS@CNT solution was pre-freeze for 30 min using liquid nitrogen, and subsequently vacuum dried at ~40 Pa for two days to sublimate the ice crystals. Then, the lyophilized sample was annealed at 500 °C for 30 min with a heating rate of 8 °C min^{-1} under the Ar atmosphere to obtain the 3D-GNS@CNT. Similarly, the 3D-GNR was prepared following the same condition using the ox-GNR as the precursor.

2.3. Characterization measurements

Field-emission scanning electron microscope (FE-SEM) images and energy dispersive spectroscopy (EDS) data of the samples were carried out on JSM-7001F SEM unit (Japan Electron Optics Laboratory Co., Ltd, Japan). Transmission electron microscopy (TEM) and high resolution TEM (HR-TEM) images were conducted under a TecnaiG^2 20ST (T20) (FEI corporation, USA) at an acceleration voltage of 120 kV. X-ray Photograph electron spectroscopy (XPS) data were carried on an ESCALab220i-XL electron spectrometer (VG Scientific Co., Ltd, UK) using 300 W AlK irradiation. The base