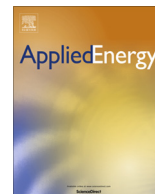




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Scalable synthesis of functionalized graphene as cathodes in Li-ion electrochemical energy storage devices

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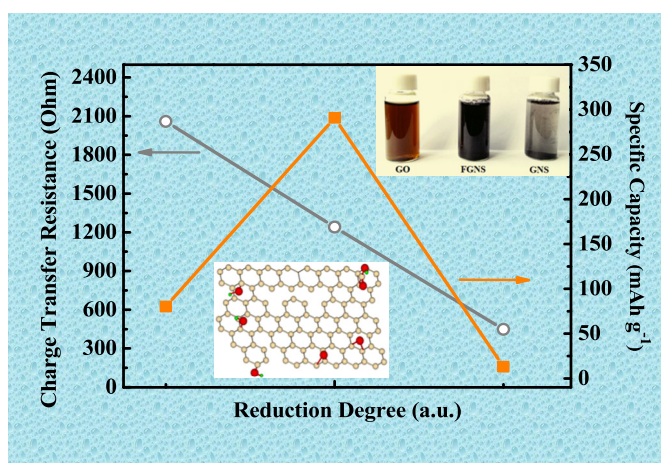
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HIGHLIGHTS

- The functionalized graphene nanosheets (FGNS) were synthesized.
- The functionalized graphene cathode showed high specific capacity and excellent cyclability.
- Oxygenic functional groups act as active sites for lithium storage.
- The proposed route exhibited some promising possibilities for mass production.

GRAPHICAL ABSTRACT



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ABSTRACT

It is highly desirable to develop high-performance and cost-effective cathode materials for lithium-ion batteries (LIBs). In this work, functionalized graphene nanosheets (FGNS) were facilely synthesized utilizing ethylene glycol as both reducing agent and solvent. When employed as cathode materials for LIBs, FGNS were demonstrated to exhibit superior electrochemical performance when compared with traditional metal oxide-based cathodes. For instance, FGNS deliver outstanding cycle stability and high specific discharge capacity of 280 mA h g⁻¹ at 0.05 A g⁻¹ without obvious capacity fading after 300 cycles. Furthermore, FGNS reveal high rate capacity of 152 mA h g⁻¹ at a high current density of 0.4 A g⁻¹. The excellent electrochemical performance is attributed to the oxygen-containing functional groups and specific porous structure of FGNS. The proposed FGNS are expected to be a simple, low-cost, efficient, and large-scale production of cathode materials for LIBs.

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1. Introduction

Energy conservation and environment protection have become important topics in the energy field. During various sustainable devices for energy storage and conversion, secondary lithium ion batteries (LIBs) with high energy density, long cycle life and environmentally benign characteristics are highly desired as potential power sources for portable electronic devices, electric vehicles (EV) and smart electricity grid [1–4]. But the current LIB technology does not satisfy the increasing demand of miniaturization of power sources for electronic devices and does not address the need for faster charging electric vehicles, especially current electric vehicles utilizing LIBs as power source are hindered by short range and long charging time, which degrades the user experience and hinders the large-scale development of EV [5,6]. To increase the capacity, lifecycle, and rate capability of LIBs, strategies include to improvement of the current electrode materials as well as proposing new cathode materials for the next generation rechargeable LIBs with high performance [7]. The attractive merit is that the commercial graphite anode actually delivers the high energy capacity of more than 330 mA h g^{-1} (372 mA h g^{-1} theoretically) [8,9]. However, the common inorganic intercalation cathode materials (e.g., LiCoO_2 , LiFePO_4 or $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$) reveal some severe drawbacks such as low practical capacity ($\sim 170 \text{ mA h g}^{-1}$) in all cases, unreliable safety in the case of LiCoO_2 , as well as the relatively high cost of cobalt (Co) and limited mineral resources for LiCoO_2 and $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ [5,10]. As a result of the low capacity, the incorporation of the cathode material is always double the anode material, which limits further improvement of battery performance. Therefore, so far, to significantly improve the cathode performance has been proven to be a challenge. Recently, three-component layered oxide systems in the form of $\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$ (NCM, $0 \leq x, y, z < 1$) and Ni-based layered oxide systems in the form of $\text{LiNi}_{1-y-z}\text{Co}_y\text{Al}_z\text{O}_2$ (NCA, $0 \leq y, z < 1$) have exhibited promising alternatives as cathode materials to substitute for LiCoO_2 , but for long-term cycling, some problems such as electrolyte decomposition and dissolution of transition metals occur at the electrode–electrolyte interface, which will lead to poor cycling stability and uncontrolled voltage changes [11–14]. For instance, the $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ studied shows limited applications in EV systems owing to its poor rate capability as well as poor stability in a high temperature environment of $55 \text{ }^\circ\text{C}$ [15]. Another developmental layered Li-rich materials can deliver a reversible capacity of more than 200 mA h g^{-1} when charged to 4.5 V, but they suffer from obvious voltage changes and inferior rate capability upon cycling [16]. Hence, new advanced cathode materials that demonstrate high reversible capacity while having superior cycling stability and low-cost are highly desirable.

Recently, the proposed replacement of the lithium metal oxide cathodes by graphene may, in principle, allow high cycling stability of Li electrochemical storage devices with high energy and power density [17,18]. High aspect ratio, good electrical conductivity and high surface area of the two-dimensional structure of graphene nanosheets [19,20] contribute to enhancing electrochemical performance when employed as cathode materials for both LIBs and supercapacitors [21–23]. A host of studies have demonstrated the pivotal role of oxygenic functional groups, which serve as active sites for lithium storage during the charge–discharge process based on the electrochemical reaction: $\text{>C=O} + \text{Li}^+ + \text{e}^- \leftrightarrow \text{>C-O-Li}$ [23–28]. Both organic cathode materials, typically organic carbonyl compounds, and graphene-based cathode materials, such as reduced graphene oxide and functionalized carbon nanotubes [29–31], deliver higher energy capacities than inorganic metal oxide cathodes [32,33]. Unfortunately, organic cathodes show poor electrochemical performances due to their poor

electrical conductivity and chemical stability in the electrolyte, which provides organic cathodes less superiority when compared with lithium metal oxide cathodes. Graphene-based cathode materials, on the other hand, exhibit great potential as transition-metal-free and cost-effective cathodes due to excellent cycling stability and high energy density/power density. However, as previously reported, the synthesis of a functionalized graphene cathode is generally based on tedious chemical reduction with low yields, such as annealing in specific atmosphere [25,34], or with a selective reduction in the organic solvent but with a relatively low energy density [35], which shows some difficulties in scale-up of the promising cathode materials.

In this study, we present a novel strategy for the fabrication of functionalized graphene nanosheets (FGNS) by partial reduction of the oxygenic functional groups of graphene oxide (GO). The FGNS proved to be superior cathode materials, which manifests high Li storage properties, superior rate capability and excellent cycling stability. The enhanced electrochemical performance was mainly owing to the lithium storage capacity of abundant oxygenic functional groups on the planes or edges of graphene nanosheets together with a highly conductive porous graphene framework. It is worth noting that during the process of partial reduction, non-toxic and low-cost ethylene glycol was used as a reducing agent and solvent at low temperature of $\sim 120 \text{ }^\circ\text{C}$, and during the separation of final product and cheap-nontoxic reductant, physical sedimentation method was adopted instead of other complicated methods such as filtration and centrifugation. Therefore, this proposed facile method shows some promising possibilities for mass production, and opens an opportunity to develop this potential cathode materials a new cathode material for high performance LIBs.

2. Experimental

2.1. Chemicals

Natural graphite powder (purity $\geq 99.95\%$) was supplied by the Aladdin Chemistry Co., Ltd. Concentrated sulfuric acid (95–98%), fuming nitric acid (65–68%), KMnO_4 (99%), NaNO_3 (99%), H_2O_2 (30%) and ethylene glycol (99.5%) were used as received from Tianjin Jiangtian Chemical Research Institute.

2.2. Materials synthesis

First, graphite oxide (GO) was prepared from natural graphite by a modified Hummers' method as reported in our previous work [36]. Next, FGNS was synthesized using GO as raw material and ethylene glycol as solvent agents. In a typical process, 2 mg mL^{-1} solution (100 mL) of graphene oxide in ethylene glycol was made from GO by ultrasonic cell disruption for 40 min. The obtained graphene oxide dispersion was then subjected to centrifugation at 10,000 rpm for 30 min to remove some non exfoliated GO (usually no more than 3 wt.%). The obtained dispersion was then transferred into a 150 mL beaker followed by heating at $120 \text{ }^\circ\text{C}$ with an oil bath for 12 h under vigorous stirring. After the reaction mixture was naturally cooled down to room temperature, the reaction mixture was subsequently poured into plenty of water to obtain black deposit. The resultant black precipitation was then repeatedly washed with deionized water, and finally the obtained black precipitation was freeze-dried to obtain FGNS. Dried FGNS powder was then charged into a quartz tube and annealed under $\text{Ar}/5\%\text{H}_2$ atmosphere at $900 \text{ }^\circ\text{C}$ for 2 h with a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$, the obtained product with removal of the most residual oxygenic functional groups was marked as GNS.

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