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Preparation, characterization and electrochemical properties of a graphene-like carbon nano-fragment material

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A B S T R A C T

A graphene-like nanomaterial, carbon nano-fragments (CNFs), is obtained using the graphite anodes of spent lithium-ion batteries (LIBs) as carbon source, and its morphology, structure, functional groups, and reactivity are characterized to evaluate the properties and potential applications. The interlayer space increase, layer distortion, and remnant lithium of the waste lithium-intercalated graphite are utilized to prepare the oxidized CNFs (ox-CNFs) through a chemical oxidation and ultrasonic crushing process. These ox-CNFs exhibit a size distribution of 15 nm to 2 μm and excellent hydrophilicity, and disperse well in an aqueous suspension. Under the hydrothermal condition at 180 °C for 12 h, the ox-CNFs are converted into a suspension of reduced CNFs (re-CNFs), or a cylindrical aggregate when the concentration exceeds $2 \, mg \cdot mL^{-1}$. The spectroscopic results demonstrate that there are abundant edges, defects, and functional groups existing on the CNFs, which affect their reactive, electronic, and electrochemical properties. Thereinto, the vacuum-dried ox-CNFs film can be converted from an insulator to a conductor after a chemical reduction by hydroiodic acid. And the re-CNFs modified glass carbon electrode (re-CNFs/GCE) exhibits enhanced electrocatalytic activity of about 8 times than the GCE to the oxidation reaction of dopamine. Furthermore, with the addition of the carboxylic ox-CNFs in aniline, the CNFs/polyaniline composite discharges a capacitance of $356.4 \, F \cdot g^{-1}$ at $2 \, mV \cdot s^{-1}$, an increase of 80.5% compared to the polyaniline. This preparation entails not only novel carbon nanomaterials but also an excellent disposal method of spent graphite, showing special significance in materials innovation and environmental science.

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1. Introduction

Along with the discoveries of carbon nanotube, fullerenes, and graphene [1,2], the insight on the properties of carbon nanomaterials has been greatly promoted. And these carbon nanomaterials have also been applied to various fields such as energy, environment, and materials based on their unique nanostructure and properties [3,4]. The applications of these known materials not only enrich the knowledge of carbon nanomaterials but also encourage the expectation of other novel nanomaterials [5,6]. Thereinto, as a basic carbon material and the raw material of carbon nanomaterials, graphite has been largely used as the active material in the anodes of lithium ion batteries (LIBs) during the past two decades. In view of the merits of high energy density, better safety feature, and more excellent cyclability, the LIBs have been widely used as power sources in mobile telephones, personal computers, video cameras and other modern appliances [7,8]. At the same time, an equal quantity of spent LIBs, which usually contains chemical substances such as copper, aluminum, cobalt, lithium, carbon, and organic electrolyte, are produced [9,10]. The recycling of the major components from spent LIBs is thus an alternative source of valuable materials and a preventative measure against the environmental pollution. Up to now, many processes concerning the recycling of spent LIBs have been proposed, especially for the recovery of cobalt, copper and lithium [11,12]. However, there are few reports devoted to recovering the graphite anode active materials of spent LIBs. It is noted that when the graphite anode material undergoes a repeated Li^+ intercalation-deintercalation process during the charge-discharge cycling of the LIBs, the change occurred in the perfect layered structure of the graphite is similar to the breaking up of the Van der Waals forces when synthesizing graphene oxide. Thus, it is believed that reclaiming the graphite material in spent LIBs may also provide a method to prepare the graphene-like carbon nanomaterials besides the innocuous treatment of the waste graphite anodes.

The reason for the lack of information on the recycling of the graphite anodes of spent LIBs may be ascribed to a lack of value and the plentiful supply of low-cost graphite raw material. However,

in practice, the unceasing accumulation of spent graphite active materials cannot be neglected from an environmental viewpoint, and the remaining lithium in the active materials must also be considered. Because the perfect layered structure of spent graphite material have been changed, and an uncertain amount of lithium ions remains in the graphite lattice voids, the direct reuse of spent graphite as the active material to produce the LIBs is not currently feasible, even after a regeneration of the graphite. In addition, the uncertainty of the lifetime and condition of the spent LIBs collected from different sources must be faced, which complicates the reclamation of the graphite anodes of spent LIBs. So, it is considered to be an optional way to produce carbon nanomaterials by using the waste graphite as raw material because the products usually aren't sensitive to the uncertainty of the graphite raw materials.

Recently, based on the structure change of the graphite material in spent LIBs, the preparation of carbon nano-fragments (CNFs) [13] and carbon dots [14] from the lithium-intercalated graphite of LIBs has been investigated by using a ball milling and an ultrasonic exfoliating process, respectively. But low yields and mass recoveries were faced when these techniques were carried out. In order to improve the reclamation efficiency of waste lithium-intercalated graphite, a chemical oxidation, known as the modified Hummers' method to prepare graphene oxide [15], was combined with an ultrasonic crushing treatment to disrupt the structure of the waste graphite particles. It has been demonstrated that nearly all of the waste graphite particles from the spent LIBs could be transferred to the graphene-like oxidized CNFs (ox-CNFs), and subsequently, to the reduced CNFs (re-CNFs) [16]. These CNF nanomaterials exhibited a unique nano-fragment appearance, abundant functional groups, and excellent electrocatalytic oxidation activity. In contrast to the well-known graphene, these CNFs can be facilely produced on a large scale although they have irregular appearance and different functional groups. Therefore, the preparation of the CNFs from the graphite anodes of spent LIBs results in not only a novel nanomaterial but also the disposal of the graphite in spent LIBs. Namely, this procedure is of special significance in materials innovation and environmental science. In this study, the detailed procedure using the graphite anodes in spent LIBs to prepare the ox-CNFs through a chemical oxidation and ultrasonic crushing process, and the hydrothermal and chemical reduction of the ox-CNFs to prepare the re-CNFs are presented. In addition, the morphology, structure, and functional groups of the as-prepared CNFs are systemically characterized, and their potential applications in the electronic, electrocatalytic, and electrochemical energy-storage fields are evaluated as well.

2. Experimental

2.1. Materials and chemical reagents

The spent rectangle-type LIBs with an initial capacity of approximately 750 mAh that were charge-discharged at 1 C for 400 cycles and dimethyl carbonate (DMC) solvent used in this work were kindly provided by Guangzhou Tinci Materials Technology Co. Ltd. The LIBs consisted of $LiCoO_2$ pasted on aluminum foil, graphite particles pasted on copper foil, 1 mol·L^{-1} $LiPF_6$/carbonates ethylene and ethyl methyl carbonate (1:2, by weight) organic electrolyte and polypropylene separator. In addition, the pristine graphite powders, i.e. the commercial natural graphite active material, used in the preparation of LIBs were also obtained from Tinci Company, and their properties were compared with the recycled graphite from the spent LIBs. Other chemical reagents, including dopamine, aniline, sulfuric acid, potassium permanganate, hydroiodic acid, and etc., were all of analytical grade and used as received.

2.2. Preparation procedure

The graphite anodes were separated from the other substances of spent LIBs and rinsed by DMC to remove residual electrolyte, and then the graphite particles were peeled from the copper substrates. After completion of the washing and drying, the obtained graphite particles were subjected to an oxidation treatment, referring to the Hummers' method in the preparation of graphene oxide [15,17], in the sulfuric acid and potassium permanganate solution. The oxidized products were ultrasonically crushed and subsequently dialyzed in a dialysis bag (retained molecular weight: 14000 Da) for 12 h to remove the impurities, and then centrifuged at 4000 rpm for 10 min to separate the large particles. The small amount of the centrifugal precipitate was returned to the above oxidizing step for further oxidation, while most of the material, which is ox-CNFs, was obtained from the centrifugal suspension. The re-CNFs could be obtained through the hydrothermal reduction of the aqueous dispersion of the ox-CNFs. The hydrothermal experiments were carried out by sealing the ox-CNFs aqueous dispersion in a Teflon-lined autoclave at 180 °C for 12 h, and the autoclaves were naturally cooled to room temperature after the reaction.

2.3. Apparatus and analysis methods

The morphology of the as-prepared CNFs was characterized by transmission electron microscopy (TEM, JEM-2100, Japan), scanning electron microscopy (SEM, ZEISS Ultra 55), and atomic force microscopy (AFM, Cypher, Asylum, U.S.). X-ray powder diffraction (XRD) measurements were carried out on a Bruker D8 Advance X-ray diffractometer (CuKα, λ=1.54178 Å). Fourier transform infrared (FT-IR) spectra of the CNFs were recorded on a Fourier transform spectrometer (TENSOR27, Bruker, Germany). Raman spectroscopy was performed using a micro-Raman system (LabRAM HR800, Horiba Jobin Yvon) with a 532 nm excitation laser. X-ray photo-electron spectroscopy (XPS) of the vacuum-dried ox-CNFs film and the freeze-dried re-CNFs was performed on an ESCALAB 250 photoelectron spectrometer (Thermo Fisher Scientific, USA) with Al Kα (1486.6 eV) as the X-ray source. Ultraviolet-visible (UV-vis) spectra were recorded by a UV-vis spectrophotometer (UV-1800, Shimadzu, Japan). The ultrasonic conditions for the separation of the waste graphite particles from the copper substrates and the ultrasonic crushing of the oxidized graphite particles were supplied by an ultrasonic cleaner (200 W, SB-520DTD, SCIENTZ, China) and an ultrasonic pulverizer (650 W, JY92-IIN, SCIENTZ, China), respectively.

2.4. Electrode preparation and measurements

The electronic conductivity of the as-prepared CNFs was evaluated by using a self-constructed circuit. By pouring the ox-CNFs suspension into a beaker and then drying in the vacuum oven, a brown compact transparent ox-CNF film of about 0.1 mm thickness was prepared. Afterwards, two pieces of ox-CNF film were cut, and one was chemically reduced through immerging into the hydroiodic acid solution (0.5 mol L^{-1}) for 1 min to prepare the re-CNF film. Then, the ox-CNF film and the re-CNF film were respectively contacted into a home-made circuit with lamp to measure their electronic conductivity.

The electrocatalytic property of the CNFs was measured by using the electrochemical oxidation reaction of dopamine in a 0.1 mol L^{-1} phosphate buffer solution (pH=7.2) at the re-CNFs modified-glassy carbon electrode (re-CNFs/GCE). The electrochemical energy-storage properties of the CNFs were characterized by measuring the capacitance of the CNFs/polyaniline composite electrodes in 1 mol L^{-1} H_2SO_4 solution. All electrochemical experiments were carried out using a CHI 660B electrochemical