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Two-dimensional hierarchical porous carbon composites derived from corn stalks for electrode materials with high performance

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ABSTRACT

Herein, we propose a novel and green strategy to convert crop stalks waste into hierarchical porous carbon composites for electrode materials of lithium-ion batteries. In the method, the sustainable crop stalks, an abundant agricultural byproduct, is recycled and treated by a simple and clean chemical activation process. Afterwards, the obtained porous template is adopted for large-scale production of high-performance anode and cathode materials for lithium-ion batteries. Due to the large surface area, hierarchical porous structures and subsize of the functional particles, the electrode materials manifest excellent electrochemical performance. In particular, the prepared TiO_2/C composite presents a reversible specific capacity of 203 mAh g^{-1} after 200 cycles. Our results demonstrate that the sheetlike composites show remarkable cycling stability, high specific capacity and excellent rate ability, and thus hold promise for commercializing the high-performance electrode materials as the advanced lithium-ion batteries.

1. Introduction

With the growth of population and economic, there demand of energy is increasing. This fact, coupled with depleting resources and increasing environmental concern, calls for sustainable energy strategy. At the moment, renewable, sustainable energy is often dependent on discrete natural energy sources, for example, hydroenergy, wind, tidal and geothermal energy. For better utilization of such non-continuous energy, it is very urgent to develop high-efficient energy-storage systems. Up to now, the lithium-ion batteries (LIBs) appear to be the attractive choice. In the past several decades, LIBs have dominated the market of portable devices, such as computer, telecommunication equipment [1–3]. The current research hotspot of new generation high performance LIBs mainly focus on the environment-friendly and high abundance electrode materials. However, most electrode materials, such as $LiFePO_4$, $LiMnPO_4$, TiO_2, Sn and S, suffer from some inherent defects, for example, low electronic conductivity and large volume expansion during lithium extraction and insertion [4–6]. For the sake of overcoming the above-mentioned disadvantages, many methods, such as coating a conductive layer on active materials, guest ion doping and fabricating nanostructures with short ion pathways, have yet been adopted to improve the electrochemical performance of electrode materials [7–10]. As one of the most effective and common strategy, carbon coating could play a vital role in commercializing the high-performance electrode materials for the advanced lithium-ion batteries. In this regard, carbon composites derived from low-costing regenerative resources will have tremendous potential in the practical applications.

Corn has long been one of the greatest botanical riddles across the world (8.504×10^8 metric tons per year) [11]. In addition, the current applications of the crop stalks have been very limited to the lowly-added-value fields, for instance fodder, fertilizer or producing furniture. As is known to all, the major ingredients of crop stalks are cellulose, hemicellulose and lignin [12]. One promising utilization method of cellulose biomass is to produce sustainable bio-fuels as alternative energy for fossil fuel. The other application method is to supply reproducible raw materials for the manufacture of chemical products, such as surfactants, pigments and polymers [13]. However, transforming of biomass into renewable carbon material in a low-cost manner attracts growing attention. Sorts of carbon materials derived from biomass (*e.g.* wheat straw, sugar cane bagasse, silk, chopsticks, banana fibers, fish scale) have been investigated for supercapacitor and LIBs [14–19]. For instance, Jiang's group adopted chopsticks as precursors to prepare uniform carbon fibers, and then grew nanostructured metal oxides

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to form core-shell electrode architecture [19]. Hou et al. fabricated hierarchical nanoporous carbon nanosheets by combinative activation and graphitization of biomass derived natural silk. The carbon material exhibited a capacitance of 242 $F g^{-1}$ and energy density of 102 W h kg^{-1} [15]. However, to the best of our knowledge, there is almost no report to introduce a general strategy to prepare 2D hierarchical porous carbon composites for both high performance anode and cathode. In contrast, as illustrated in our paper, we have successfully fabricated both cathode and anode materials for LIBs, for instance, $LiMnPO_4$ and TiO_2.

In this paper, we utilize crop stalks as precursors to prepare two-dimension hierarchical porous carbon composites for high performance batteries anode and cathode, in which the porous carbon nanosheets serve as host carbon matrixes for functional nanoparticles. As shown in Fig. 1, to begin with, chemical activation is applied to obtain the 2D nanostructural carbon-based materials with hierarchical pores and high specific surface area [20,21]. The metal salts $FeCl_3$ and $ZnCl_2$ not only facilitate dissolution of natural corn stalks but also act as effective activation graphitization agents which can introduce a porous nanostructure with plentiful micropore and mesopore for large surface areas [15]. Afterwards, the functional particles are embedded into the porous carbon sheets via a reported infusing process, followed by calcinations in an inert atmosphere [22,23]. Finally, we obtain 2D hierarchical porous sheetlike carbon composites, in which functional materials are embedded. Compared with other carbon composites derived from natural bio-polymeric and traditional synthetic method for Li-ion batteries, our strategy has several advantages as follows: 1) In the previous studying, nearly all the works concentrate on anode materials such as Si [24,25], S [26], MnO_2 [19] and C [15,16,27]. In contrast, we have expanded this general synthetic method based on bio-feed stock from elementary substance or metal oxide to complex compound. It should be highlighted that the method applied here is facile and universal. In addition, this general synthetic method is easy to extend to fabricate other electrode materials for LIBs. 2) Several biomass resources, for example, silkworm, banana fibers, fish scale, coconut shell, wheat straw, chopsticks, rice husk *etc.* have been used to create carbon as electronic conductors for electrode materials [14–19]. Obviously, the biomass sources mentioned above have scarce reserves on the earth, compared to the corn stalks. Therefore, the strategy using crop stalks has broader applicative prospect. 3) The corn stalks possess natural sheet-like cellulose, providing sacrifice template and carbon source for the as-prepared products. 4) The chemical activation employed in the strategy not only provides high specific surface for active sites but also introduces hierarchical porosity (intertwined micro-, meso- and macropores). The porous structure not only provides more bonding sites but also increases the contacting areas between active material and electrolyte, which in turn enhances the cycling ability and rate ability of electrode materials [28]. 5) The 2D porous carbon composites could shorten the diffusion pathways of lithium ion and provide shorted diffusive resistance of mass transport on a large electrode/electrolyte interface [29,30]. Moreover, the naturally nanoporous sheetlike carbon matrix stemming from crop stalks is capable to prevent the nanoparticles from aggregation as well as an elastic buffer to remit the mechanical strain during lithium ion insertion/extraction. In brief, the facile fabrication strategy is beneficial to generating high-performance electrode materials for LIBs, which have a highly reversible specific capacity, excellent rate ability and remarkable cyclability.

2. Experimental Section

2.1. Chemical activating of corn stalks

Five grams of natural corn stalks without any further treatment was mixed with 2.5 g of $ZnCl_2$ in a 2.5 M (10 mL) $FeCl_3$ solution as an initial step. The solution was continuously stirred and evaporated at 70 °C for 4 h. Then the activated corn stalks were washed by 1 M hydrochloric acid for at least three cycles and for three cycles using deionized water. Activated crop stalks were obtained by further drying at 80 °C in a conventional oven. For obtaining porous carbon nanosheets, the activated crop stalks were calcined at 800 °C for 200 min under Ar atmosphere with a ramp of 5 °C min^{-1}.

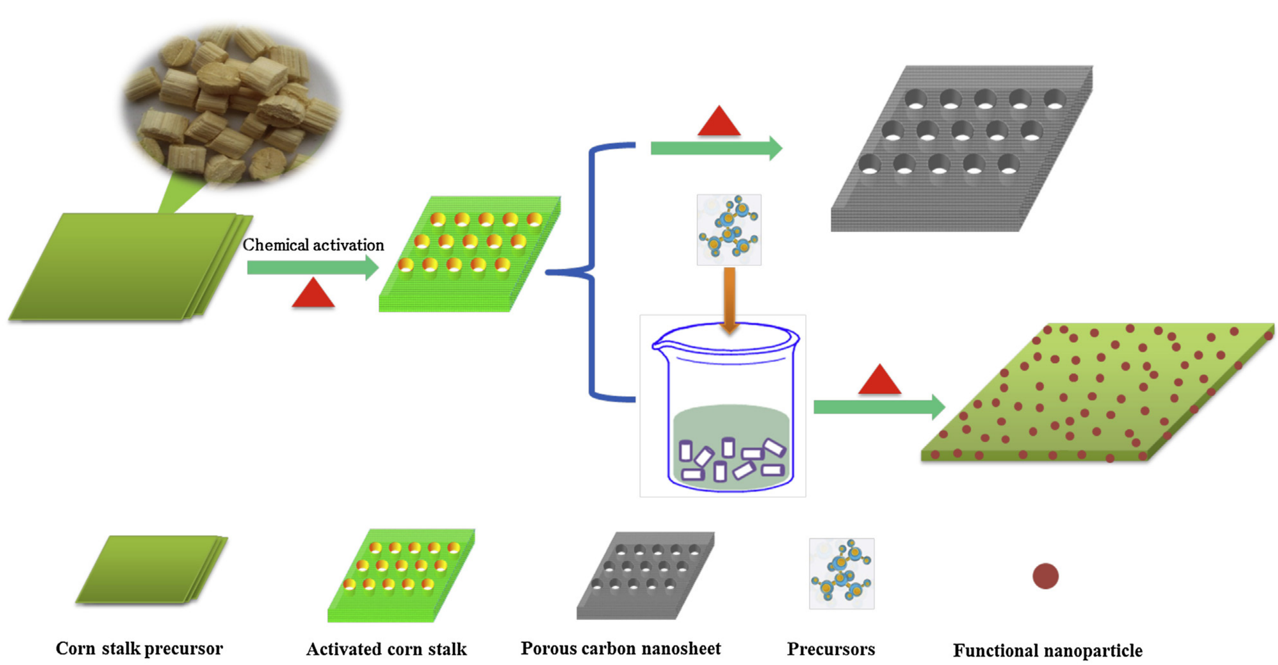

Fig. 1. Schematic illustration of the synthetic strategy for the production of 2D hierarchical nanoporous carbon composites.