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Synthesis of porous graphene/activated carbon composite with high packing density and large specific surface area for supercapacitor electrode material

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HIGHLIGHTS

- Porous graphene/activated carbon was prepared via hydrothermal carbonization and subsequent two-step chemical activation.
- The composites owe a high packing density and has a specific capacitance of 210 F g^{-1}.
- A high capacity retention rate of 94.7% after 5000 cycles can be achieved.

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ABSTRACT

A simple method has been developed to prepare graphene/activated carbon (AC) nanosheet composite as high-performance electrode material for supercapacitor. Glucose solution containing dispersed graphite oxide (GO) sheets is hydrothermally carbonized to form a brown char-like intermediate product, and finally converts to porous nanosheet composite by two-step chemical activation using KOH. In this composite, a layer of porous AC coats on graphene to from wrinkled nanosheet structure, with length of several micrometers and thickness of tens of nanometer. The composite has a relatively high packing density of ~0.3 g cm^{-3} and large specific surface area of 2106 m^2 g^{-1}, as well as containing plenty of mesopores. It exhibits specific capacitance up to 210 F g^{-1} in aqueous electrolyte and 103 F g^{-1} in organic electrolyte, respectively, and the specific capacitance decreases by only 5.3% after 5000 cycles. These results indicate that the porous graphene/AC nanosheet composite prepared by hydrothermal carbonization and chemical activation can be applied for high performance supercapacitors.

1. Introduction

Supercapacitor – also called electrochemical capacitor – is a new electrochemical energy storage system applied for harvesting energy and delivering high power in short time. Its main energy storage mechanism is based on charging an electrical double-layer (EDL) at the electrode–electrolyte interface of high surface area electrode materials. They have attracted attention for a variety of applications, especially in hybrid systems combining with batteries and fuel cells, due to their high power density, excellent cyclic stability and rapid response to external loading on a powertrain [1–4]. Nevertheless, the main disadvantage of supercapacitor is the relatively low energy density (5–6 Wh kg^{-1} based on activated carbon, AC), which is significantly lower than that of lithium ion rechargeable battery (~150 Wh kg^{-1}). Therefore, the most important issue for supercapacitor research is to enhance its energy density. Many efforts have been focused on developing new kinds of electrode materials, such as carbon nanotubes (CNTs) [5,6], graphene [7,8] and CNTs/graphene hybrid materials [9,10], as well as transition metal oxides [11,12] and conductive polymers [13–15] having pseudocapacitive behaviors. Unfortunately, up to now only AC has been commercially used as supercapacitor electrode materials due to its well-developed microstructure, high specific surface area, relatively high packing density, and low cost. However, their applications account for only a comparatively small market because of its low energy density. On the other hand, the AC particles usually have sizes up to several tens of micrometers, which results in a long diffusion pathway for ions, as well as relatively low conductivity. These disadvantages make AC unfavorable in the process of rapid charge/discharge and for the requirement of excellent cyclability. For the AC materials, to enhance surface area as well as

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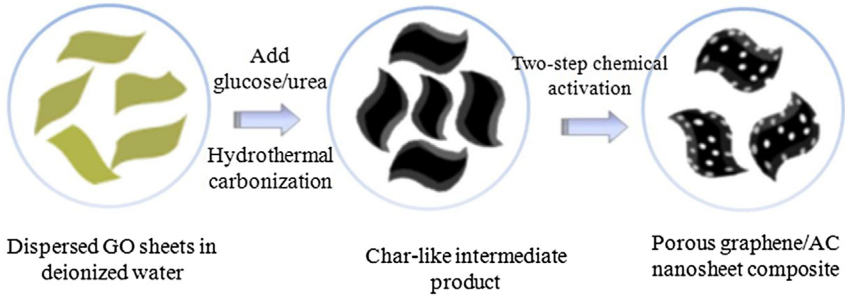

Fig. 1. Schematic illustration showing the experimental steps of preparing porous graphene/AC nanosheet composite.

maintain high packing density, control pore size distribution, reduce diffusion resistance and improve conductivity are still challenging.

Graphene [16], a two-dimensional carbon material consisting of a single-layer of sp^2 hybridized carbon atoms, has been considered as an outstanding candidate electrode material for supercapacitors due to its unique properties, such as exceptionally high specific surface area (2630 $m^2\ g^{-1}$, higher than that of CNTs and commercial AC, and major surface of graphene is exterior surface readily accessible by electrolyte), excellent electrical conductivity and stable chemical properties. Most significantly, the intrinsic capacitance of graphene was found to be 21 $\mu F\ cm^{-2}$ [17]. Thus, the theoretical value of graphene is calculated to be 550 $F\ g^{-1}$, provided the entire surface is fully utilized. Many works have been reported based on graphene and modified graphene [18–20] for supercapacitors. Unfortunately, the EDL capacitance value measured is far lower than the theoretical one, mainly because that graphene sheets have inevitable tendency to restack themselves during all procedures of graphene preparation and subsequent electrode production. Meanwhile, the low packing density with a value as low as 0.005 $g\ cm^{-3}$ is another drawback of graphene. In the past, many works were interested in the materials with high specific surface area, and the specific capacitance per unit weight is mostly adopted to judge the performance of the electrode materials. However, the specific capacitance per unit volume ($Wh\ L^{-1}$) is of prime importance for practical applications as the space for the

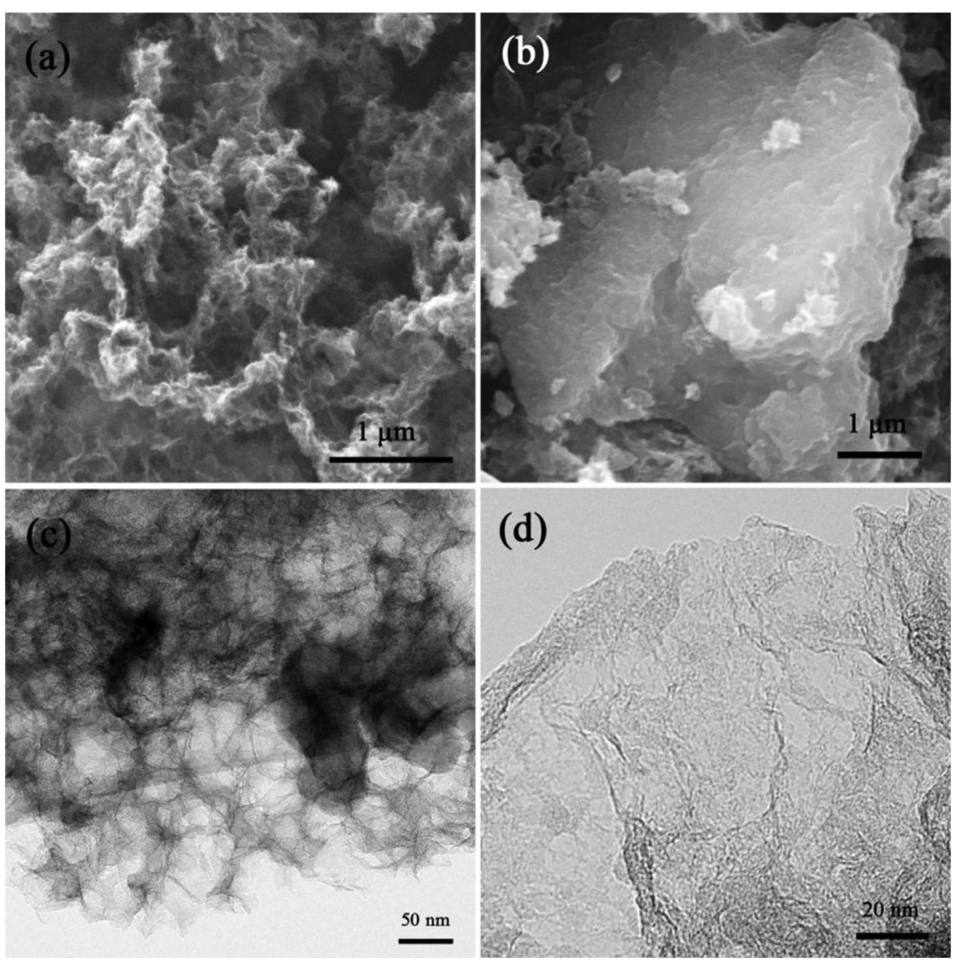

Fig. 2. (a) SEM image of char-like intermediate product, (b) SEM image of graphene/AC nanosheet composite, (c), (d) TEM images of graphene/AC nanosheet composite.