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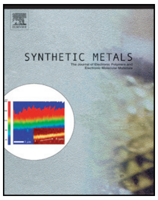

Activation of hierarchically ordered mesoporous carbons for enhanced capacitive deionization application

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ABSTRACT

In this study, an environmentally benign strategy was used to fabricate hierarchically ordered mesoporous carbons (HOMCs) using sugarcane bagasse as the scaffold and then activated with nitric acid or carbon dioxide for capacitive deionization (CDI) application. Calcium ions were selected as the model species because of the importance to hard water. The electronic microscopic images show that the HOMCs contain large domains of highly ordered hexagonal arrays of mesopores with 1-D channels and the ordered structures are retained after activation with nitric acid (HOMC-H). In addition, the oxygen and nitrogen content increase in HOMC-H. Different from HOMC-H, a partial distortion of mesostructures with the increase in micropore surface area is observed after physical activation with CO_2. The electrochemical performance of HOMCs shows ideal rectangular voltammograms with non-faradic reaction at scan rates of 1–10 $mV\,s^{-1}$ and the specific capacitance of HOMC-H is 1.4–20 times higher than those of as-prepared and CO_2-activated HOMCs. The impedance measurement shows good transport of the bulk electrolyte to the electrolyte/electrode interface of HOMC-H with excellent reversibility and ideal capacitive properties. In addition, the specific electrosorption capacity of HOMC-H electrode materials for Ca^{2+} removal can be up to 115.4 $\mu mol\,g^{-1}$ at 1.2 V. The excellent electrochemical performance of HOMC-H is mainly attributed to the increased mesoporous structures and hydrophilic functional groups after chemical activation. Results clearly indicate that the HOMC-H is a promising electrode which could facilitate good charge propagation and fast ion adsorption to treat grey and brown waters.

1. Introduction

Ordered mesoporous carbons (OMCs) have recently been regarded as the novel nanomaterials for a wide application in the fields of electrochemical adsorption, supercapacitor, lithium ion batteries, catalyst support and water purification [1–6]. Several technologies including soft and hard template methods have been used to fabricate various morphologies of OMCs [7,8], and the solvent evaporation-induced self-assembly (EISA) has been demonstrated to be a promising method for fabrication of OMCs [9]. However, the produced amounts of OMCs by EISA are usually limited and cannot provide the sufficient quantity for application. More recently, the use of natural and artificial templates including sugarcane bagasse [10], polyurethane foam [11] and crab shell [12] as the scaffolds for mass production of OMCs has been developed. Huang and Doong [13] used natural sugarcane bagasse as the sacrificial scaffold to prepare hierarchically porous carbon materials (HPCMs) and found that the bagasse-based HPCMs had a good electrochemical performance with the specific capacitances of 190–234 $F\,g^{-1}$ at the scan rates of 5–50 $mV\,s^{-1}$ in acidic solutions.

Although OMCs show good electrochemical performance on energy storage, the hydrophobic characteristics on the surface of OMCs could lower the wettability and electrolyte accessibility of OMCs, resulting in the decrease in transfer rates of electrons and ions. Several physicochemical methods have been developed to modify the surface characteristics of OMCs and chemical oxidation by oxidants such as HNO_3, H_2O_2 and $KMnO_4$ has been proven to be an effective method to introduce oxygen-containing groups including hydroxyl, carboxyl, carbonyl, lactone, and quinone groups to the surface of carbon materials [13–15]. Among the reagents used for modification, nitric acid is one of the most often used chemical because of the good ability to remove impurities on carbon surface. Tripathi et al. [16] used

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nitric acid to functionalize OMC prepared by using SBA-15 silica as the template and found that both N and O contents were increased after oxidation while ordered structures were maintained. Chou et al. [17] found that purification of single-wall carbon nanotubes by nitric acid not only increased the internal surface area but also introduced oxygen-containing surface groups.

The supply of sufficient clean water for daily demand has recently received consideration attention because of the need of industrial and agricultural activities and, therefore, the development of an efficient technology for separation and purification of water is required. Capacitive deionization (CDI) has been regarded as an energy-efficient process to remove a wide variety of ions because of the low energy consumption, low pressure demand and environmental friendliness [14,15]. Similar to the energy storage in supercapacitors, the mechanism for salt removal by CDI involves the application of an electric field to force ionic species toward opposite electrodes, and results in the accumulation of ions within the electrical double layers near the electrode surfaces [16]. The electrosorption plays an important role in determination of efficiency of CDI, and, therefore, the search of electrode materials with good pore textures and high specific surface areas is highly needed.

Activated carbons (ACs) have been widely applied as the electrode materials for supercapacitors and CDI [21]. However, the wide pore distribution may cause severe reduction in capacitance at a short current drain time [17,18]. Several graphene-based composite materials including graphene/mesoporous carbon, graphene-coated hollow mesoporous carbon and three-dimensional graphene-based hierarchically porous carbon have been developed for CDI application [19–26]. The graphene-based materials with 3-D interconnected structures and high specific surface areas can provide more adsorption sites for enhanced desalination efficiency, resulting in the improvement of electrochemical properties and the reduction of inner resistance for ion transfer. More recently, the 3-dimensional hierarchically OMC (HOMC) has been considered as a promising material for energy storage and CDI application because of its ability to reduce the resistance of electrolyte diffusions as well as to provide suitable ion transport pathway for electrolytes in hierarchical structures [27–29]. However, the application of HOMCs for CDI process to remove ions has received less attention. In addition, the activation of carbon materials with chemical reagents or CO_2 may alter the surface hydrophilicity of HOMCs, resulting in the enhancement of CDI efficiency. Therefore, it is desirable to develop a fabrication strategy for mass production and activation of HOMCs so that the carbon materials can have high specific surface area and well inter-connective pore channels to enhance the electrosorption capacity toward ion separation.

In this study, an environmentally benign strategy for the fabrication of HOMCs using sugarcane bagasse as the scaffold for mass production was developed for CDI application. Calcium ions were selected as the model species because of its importance to hard waters. The surface functionality of HOMCs was then activated with CO_2 or HNO_3 for enhanced electrocapacitive performance of CDI processes. The morphology, specific surface area, surface property and change in elements of HOMCs before and after the activation were investigated. In addition, the electroechemical performance of as-prepared and activated HOMCs was examined by using cyclic voltammetry (CV), galvanostatic charge–discharge and electrochemical impedance spectroscopy (EIS). The electrosorption capacity of as-prepared and activated HOMCs for removal of calcium ions was also evaluated.

2. Experimental

2.1. Chemicals

Phenol (99%) and formaldehyde (24 wt%) were obtained from Acros Organics (Pittsburg, PA). Absolute ethanol (99.8%) was purchased from Riedel-deHaën (Seelze, Germany). Pluronic F127 ($EO_{106}PO_{70}EO_{106}$), the amphiphilic triblock copolymer for meso-structural directing agent, was purchased from Sigma–Aldrich Co. (Milwaukee, WI). Commercial activated carbons were obtained from China Activated Carbon Industries Ltd. (New Taipei City, Taiwan). All other chemicals were of analytical grade and were used as received without further purification. In addition, aqueous solutions were prepared using bi-distilled deionized water (Millipore Co., 18.3 MΩ cm) unless otherwise mentioned.

2.2. Preparation of phenol-formaldehyde (PF) resins

The basic polymerization method was used to synthesize low-molecular-weight PF resins (MW 500–5000) in the presence of phenol and formaldehyde. Briefly, 32 g of phenol was melted at 45 °C followed by the addition of 6.8 g of 20 wt% NaOH solution under stirring conditions. After 10 min of mixing, 87.3 g of formaldehyde were added into the solution dropwise, and the mixture was stirred at 65 °C for 60 min. The pH was adjusted to 6.0–7.0 using 2 N HCl solutions after cooling down to room temperature, and then the water content was removed in vacuum at temperature lower than 50 °C. The PF resins were re-dissolved in 50 wt% of ethanol solution.

2.3. Mass production of HOMCs

Fig. 1 illustrates the mass production of HOMCs by EISA in the presence of sugarcane bagasse. The sugarcane bagasse was first sliced into the size of $20 \times 10\,mm^2$, and the mixture containing 5 g of F127 and 10 g of 50 wt% PF resins was prepared under homogeneous stirring for 1 h at room temperature. The sliced sugarcane bagasse was submerged in the mixture under stirring for 0.5 h. After infiltration, the sliced carbon materials were stood for 3 h at 25 °C and then at 50 °C for another 24 h to evaporate the

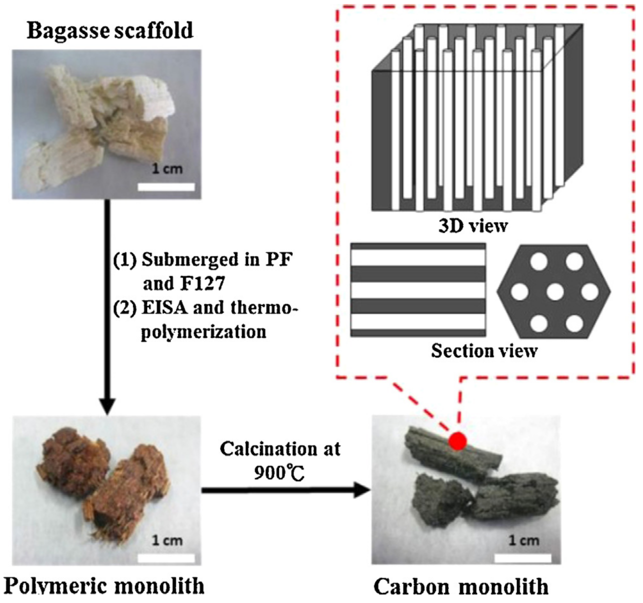

Fig. 1. Schematic illustration of hierarchically ordered mesoporous carbons (HOMCs) using sugarcane bagasse as the scaffold.