Fallen-leaf-derived microporous pyropolymers for supercapacitors

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ABSTRACT

In this study, microporous pyropolymers (GL-AMPs), a carbon-based material, were fabricated from ginkgo leaves by simple pyrolysis with KOH, followed by acid treatment. The GL-AMPs were mainly composed of aromatic hexagonal carbon layers, which were not well stacked, and contained many redox-active heteroatoms such as oxygen and nitrogen. In addition, the GL-AMPs had a high specific surface area of $\sim$1348.4 $m^2 g^{-1}$ with numerous ultramicropores ($<$0.7 nm). These unique material characteristics led to a significantly high specific capacitance of $\sim$731 $F g^{-1}$, high rate capabilities, and stable cycling performance over 1000 cycles in a redox-mediated aqueous electrolyte.

Introduction

With the rapid advancement of technology used in mobile phones, laptops, electric gadgets, and electric vehicles, rechargeable power sources exhibiting high electrochemical performances have become increasingly important [1,2]. Supercapacitors are one of the most attractive power sources in several rechargeable energy storage systems because of their high power density, great cyclic stability, and a relatively simple cell configuration [2]. The low energy density of supercapacitors, however, limits their broad applications. The energy density can be expressed as $CV_i^2/2$, where C is the capacitance and V_i is the initial voltage [3]. The capacitance is highly dependent on the active surface area, textural properties, and the presence of redox-active heteroatoms of electrode materials; therefore, the effective design of supercapacitors is key to increasing their energy density [4,5].

Porous carbon-based materials (PCMs) are conventionally used as electrode materials for supercapacitors because of their high specific surface area, high electrical conductivity, light weight, and chemical stability, and the low processing and raw material costs of the well-known technologies using them [4,5]. Activated carbon with a specific surface area of 500–3000 $m^2 g^{-1}$ has shown specific capacitance between 50 and 300 $F g^{-1}$ in aqueous electrolytes [6–12]. These capacitance values can be further increased by introducing redox-active heteroatoms on the carbon surface, which are able to store additional charges by exhibiting pseudocapacitive behavior [3–6,13,14]. In addition, sub-nanometer-scale pores can reduce the effective thickness of electrochemical double layers, leading to enhanced capacitance values in PCMs [15]. Therefore, to achieve high-energy-density supercapacitors, the desirable electrode material should have a high specific surface area, an effective pore size, and numerous redox-active heteroatoms. Moreover, by using redox-mediators in conventional aqueous electrolytes, the capacitance values can be increased even further [16–18]. Wu et al. reported that a specific capacitance of $\sim$605 $F g^{-1}$ can be achieved by adding para-phenylenediamine (PPD) in an aqueous KOH electrolyte [16], which translates to an energy density nearly twice of that of conventional supercapacitors. A synergistic energy storage effect originating from a well-developed PCM and a redox-active electrolyte could result in better electrochemical performance.

Fallen leaves constitute one of the most abundant and ubiquitous examples of waste in nature [19]. Carbon-based materials prepared from fallen leaves are cheap, sustainable, and eco-friendly; hence, they have been applied in various fields such as electrocatalysis [20], energy storage [21], CO_2 capture [22], and biosensors [23]. Textural and surface properties of the prepared carbon materials are highly dependent on the precursor material and their production process. Therefore, the reported fallen-leaf-derived carbon-based materials showed different physicochemical properties, which means that they can be used as active electrode materials for supercapacitors [24–27].

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In this study, microporous pyropolymers (GL-AMPs), a carbon-based material, are fabricated from ginkgo leaves (GLs) by controlled pyrolysis with KOH, followed by acid treatment. The GL-AMPs showed unique material properties, resulting in an exceptionally high specific capacitance of $731\,F\,g^{-1}$, high rate capabilities, and stable cycling performance over 1000 cycles in an aqueous electrolyte with PPD.

Experimental

Preparation of GL-AMPs

5 g of GLs obtained from the campus of Inha University was mixed with 10 g of KOH in a mortar by grinding for 30 min. The mixture was heated in a furnace to 800 °C under an Ar atmosphere, with a heating rate of $10\,°C\,min^{-1}$ and an Ar flow of $200\,mL\,min^{-1}$. The resulting material was washed several times with ethanol and water, and dried in an oven at 60 °C. The dried products were treated with 40 wt.% nitric acid solution under stirring at 60 °C for 3 h. Then, the as-obtained GL-AMPs were washed several times with ethanol and water, and stored in an oven at 30 °C after drying in an oven at 60 °C. GLs were heated under the same conditions, but without KOH, to produce a reference sample. The as-prepared reference sample was named GL-800. In addition, activated GLs with no acid treatment were prepared and named GL-MPs.

Characterization

The pyrolysis behaviors of the GL samples were characterized by thermogravimetric analysis (TGA, Q50, TA instruments, UK) at 800 °C at a heating rate of $10\,°C\,min^{-1}$ under a N_2 atmosphere. X-ray photoelectron spectroscopy (XPS, PHI 5700 ESCA, USA) was used to investigate the surface chemical properties of GL-800 and the GL-MPs and GL-AMPs. The morphologies of the GL-MPs and GL-AMPs were observed by field-emission scanning electron microscopy (FE-SEM, S-4300, Hitachi, Japan) and field-emission transmission electron microscopy (FE-TEM, JEM2100F, JEOL, Tokyo, Japan). Raman spectra were recorded using a continuous-wave linearly polarized laser (514.5 nm wavelength, 2.41 eV, and 16 mW power). The laser beam was focused using a $100\times$ objective lens, resulting in a spot of $\sim1\,\mu m$ diameter. X-ray diffraction (XRD, Rigaku DMAX 2500) analysis was performed using Cu-Kα radiation with a wavelength of $\lambda = 0.154\,nm$ at 40 kV and 100 mA. Pore structures were characterized by nitrogen adsorption and desorption isotherm tests using the surface area and a porosimetry analyzer (ASAP 2020, Micromeritics, USA) at $-196\,°C$.

Electrochemical characterization

The electrochemical properties of the GL-MPs and GL-AMPs were characterized by cyclic voltammograms (CVs) and chronopotentiometry (PGSTAT302N, Autolab). Ag/AgCl and Pt wires were used as the reference and counter electrodes, respectively. A 6 M aqueous KOH solution and a 2 M aqueous KOH solution containing 0.05 M PPD were used as electrolytes. The three-electrode system was tested in a beaker cell. Working electrodes were prepared by adding 5 wt.% polytetrafluoroethylene (PTFE, Sigma–Aldrich, 60 wt.% dispersion in H_2O) to the GL-MPs or GL-AMPs. The active samples and PTFE were ground into a paste using a mortar and pestle, and rolled into uniformly thick sheets (40–50 mm thickness), and punched into $1\,cm^2$ electrodes. The loading contents of the active electrode were about 3–4 mg after drying overnight at 100 °C. The specific capacitance was determined from galvanostatic measurements using the following equation:
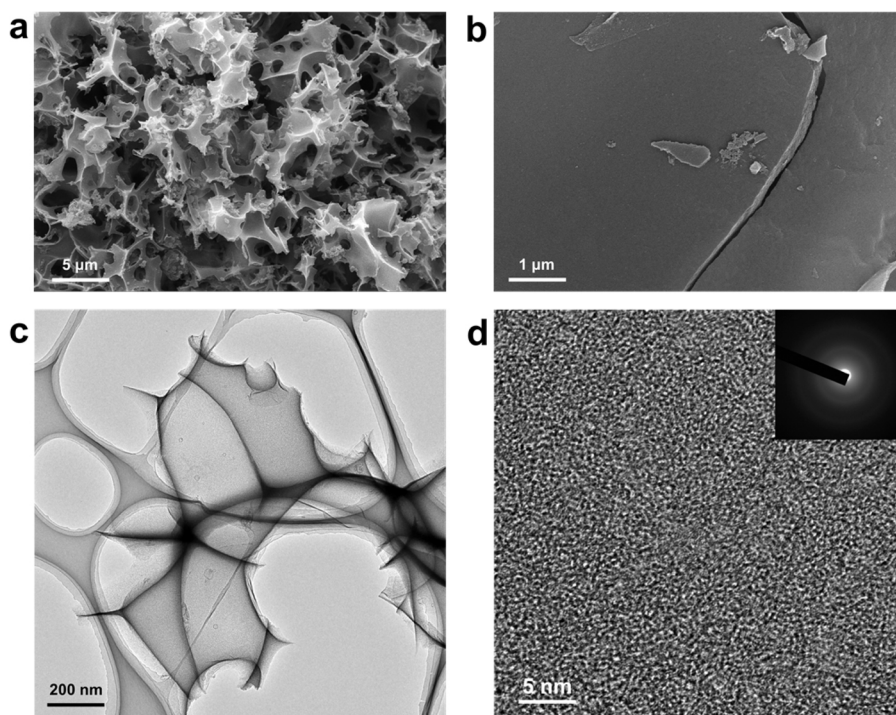
$$C = \frac{4I_{cons}}{mdV/dt},\tag{1}$$

Fig. 1. Morphological characteristics of GL-AMPs. (a) and (b) FE-SEM images of GL-AMPs at different magnifications. (c) and (d) FE-TEM images of GL-AMPs at different magnifications, and (d) (inset) diffraction pattern of the selected area.