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Biomass derived mesoporous carbon monoliths via an evaporation-induced self-assembly

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ABSTRACT

Evaporation-induced self-assembly has been applied in the synthesis of crack-free mesoporous carbon monolith with good mechanical stability using a waste plant material as carbon precursor and triblock copolymer F127 as template. The carbon monolith was characterized using transmission electron microscopy, scanning electron microscopy, nitrogen adsorption–desorption measurement, X-ray diffraction and Fourier transform infrared spectroscopy. The results showed that the carbon monolith is mesoporous, has a surface area of 219 m^2/g, and a narrow pore size distribution of 6.5 nm.

1. Introduction

Mesoporous carbon monoliths having properties such as high thermal stability, high surface area and chemical inertness are very attractive for applications in many fields such as adsorption, catalysis, energy storage and separation [1,2]. However, the available methods for the synthesis of carbon monoliths are very expensive. For example, the traditional method for the synthesis using mesoporous silica materials as “hard template” [3–5] is costly and involves a lot of steps to prepare the scaffolds which are usually sacrificed with the surfactant templates [6]. The “soft-template” method which is a method of organic-organic self-assembly involving the use of a polymerizable precursor and block copolymer templates is expected to be more flexible and has been applied by many authors [6,7] via a hydrothermal approach [2,8], aqueous reaction routes [9] and the evaporation-induced self-assembly (EISA) [10–12]. The energy requirement and the cost of the carbon precursors also make this method expensive. It is therefore important to look for a cheaper alternative for the synthesis of carbon monoliths.

The production of porous carbon materials from cheap naturally occurring precursors through environmentally friendly processes is a hot topic in modern materials science research [13]. This study presents a novel concept whereby a readily available and sustainable organic waste material is used as the precursor for the synthesis of a carbon monolith. The preparation of the material was based on the evaporation-induced self-assembly method described by Liu et al. [6]. The method produces carbon mesostructures of uniform pore size and substantially high surface area utilizing a triblock copolymer F127 as the template and organic precursors. Our study aims to provide a cost effective strategy for the production of advanced material through a green process which scales down and minimizes the volume of chemicals used by converting waste material into a useful product. To the best of our knowledge, this is the first time waste plant material has been used as the carbon precursor in the synthesis of a carbon monolith through evaporation-induced self-assembly, avoiding the energy intensive requirements of the other processes.

2. Experimental

Ethanol and HCl (analytical grade) were used without further purification. Triblock copolymer Pluronic F127 ($EO_{106}PO_{70}EO_{106}$) was purchased from Sigma-Aldrich, UK. The *Prosopis africana* shell is a waste plant material from Nigeria. It was dried, crushed and sieved to 212 μm size.

Material synthesis: The preparation of the carbon monolith was based on a modified version of the method described by Liu et al. [6]. 2.5 g of the pluronic F127 was dissolved in a mixture of deionized water and ethanol (20 ml each) and 2.5 g of *P. africana* shell was added. This was followed by the addition of 0.2 g of 37% HCl. The reaction mixture was stirred for 1 h and was left open for 72 h at room temperature for the ethanol to evaporate. The reaction mixture was transferred into a mold and dried in an oven at 50 °C for 12 h and 80 °C for 12 h. It was carbonized in a tubular furnace under nitrogen flow at a heating rate of 5 °C/min, keeping the temperature at 600 °C for 6 h to obtain the carbon monolith.

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Material characterization: Surface area, pore volume and pore size distribution were measured by N_2 adsorption–desorption isotherms using a Micromeritics Tristar BET-N_2 surface area analyzer. The morphology and particle size were visualized using a ZEISS EVO 60 scanning electron microscopy (SEM). X-ray diffraction (XRD) patterns were recorded on a Siemens D5000 powder diffractometer using a Cu Kα X-ray source. Transmission electron microscopy (TEM) images were obtained using a JEOL-2010 microscope. Fourier transform infrared (FT-IR) spectra were collected on a Thermoscientific Nicolet 380 FT-IR using KBr pellets of the solid samples.

3. Results and discussion

The plant material is used as carbon precursor in this study because the high numbers of hydroxyl groups of the oligomers present in the plant material will provide the great driving force needed for the self-assembly interaction with the polyethylene oxide (PEO) segments of the amphiphilic triblock copolymer through hydrogen bonding [14]. This factor is very important for the preferential organization of the carbon precursors according the spatial arrangement of the hydrophilic block of the F127 [6]. The oligomers in the plant material in addition, can further polymerize to thermosetting polymers with cross-linked nanostructure, resulting in high carbon content and mesoporous structure after carbonization in an inert atmosphere.

Photographs of the as-synthesized and the corresponding carbon monoliths are shown in Fig. 1a and b, respectively. Very stable carbon samples that retained the shape of the monolith were obtained after carbonization. However, the volume shrinks to about 75% of the original volume. Despite the reduction in volume during the carbonization process, the carbon monolith remained crack-free. TEM images shown in Fig. 1c and d revealed further information about the changes that took place on carbonization. The image of the carbon monolith reveals that the carbon skeleton is made up of aggregates of spherical carbon nanoparticles, resulting in the formation of mesoporous structure. Fig. 1e and f shows the SEM images of the as-synthesized and the carbon monolith, respectively. The as-synthesized monolith shows a network of fibrous structures typical of lignocellulosic material, while pores are seen on the surface of the carbon monolith resulting from the decomposition of the template (Pluronic F127) on carbonization and the changes in the plant tissue which remained as carbonaceous pore wall [7,15].

Fig. 2(a) shows N_2 adsorption–desorption isotherm of the carbon monolith, which gave further insight into the porosity of

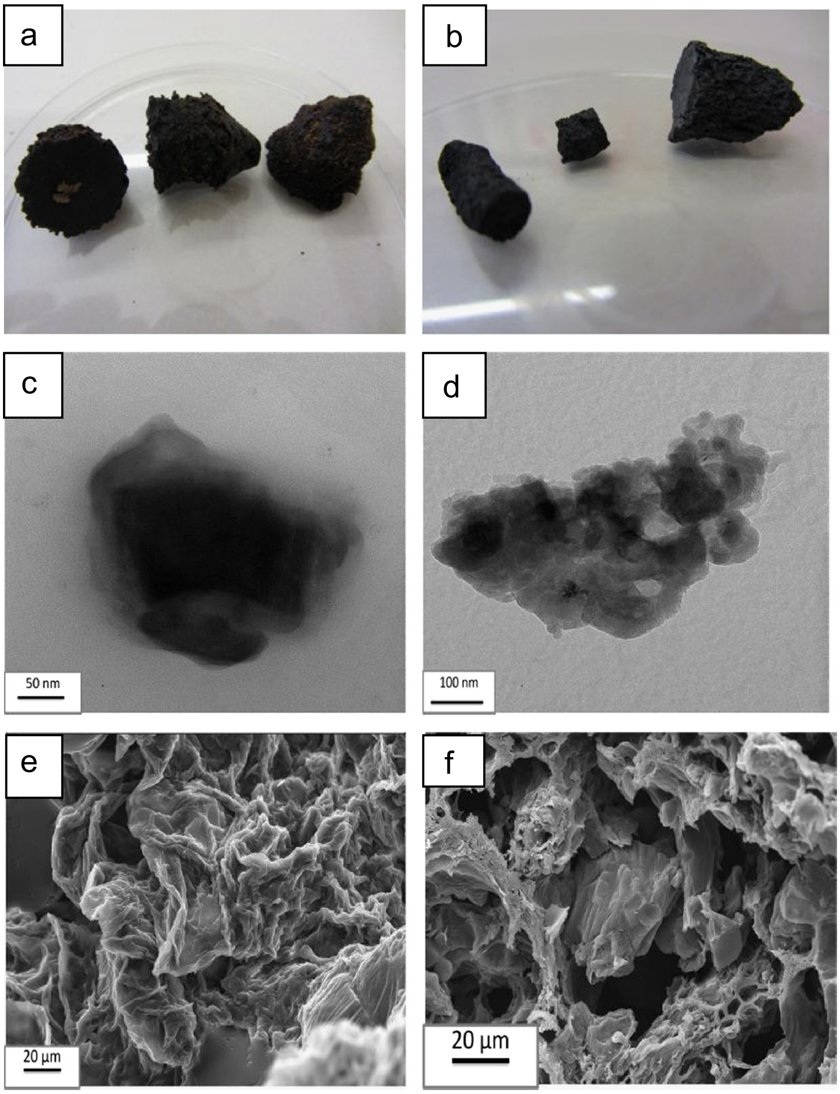

Fig. 1. (a) Photograph of as-synthesized monolith (b) photograph of carbon monolith (c) TEM image of as-synthesized monolith (d) TEM image of carbon monolith (e) SEM image of as-synthesized monolith and (f) SEM image of carbon monolith.