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

Sunday E. Elaigwu*, Gillian M. Greenway

Department of Chemistry, University of Hull, Cottingham Road, Hull, UK, HU6 7RX.

* Corresponding author. Tel: +447733680543; fax: +441482466410

E-mail: .e.elaigwu@2009.hull.ac.uk, @hotmail.com

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 /g, and a narrow pore size distribution of 6.5 nm.

Keywords: Carbon monolith, *Prosopis africana* shell, Mesoporous material, Pluronic F127

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 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 make this method to be also expensive. It is therefore important to look for 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 utilising 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 minimises 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 () 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 *Prosopis africana* shell was added. This was followed by the addition of 0.2 g of 37 % HCl. The reaction mixture was stirred for 1 hour and was left open for 72 hours at room temperature for the ethanol to evaporate. The reaction mixture was transferred into a mould, dried in an oven at 50 ℃ for 12 hours and 80 ℃ for 12 hours. It was carbonized in a tubular furnace under nitrogen flow at a heating rate of 5 ℃/min, and keeping the temperature at 600 ℃ for 6 hours to obtain the carbon monolith.

Material characterization: Surface area, pore volume and pore size distribution were measured by adsorption-desorption isotherms using a Micromeritics Tristar BET- surface area analyser. The morphology and particle size were visualised 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 organisation 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.
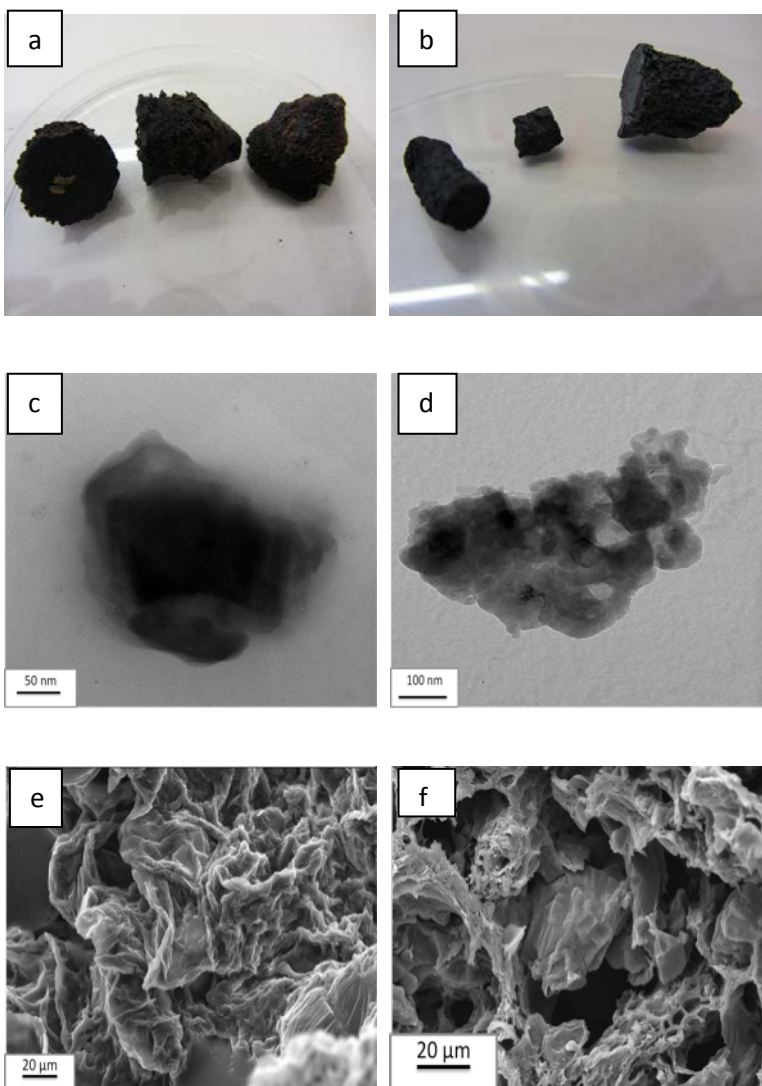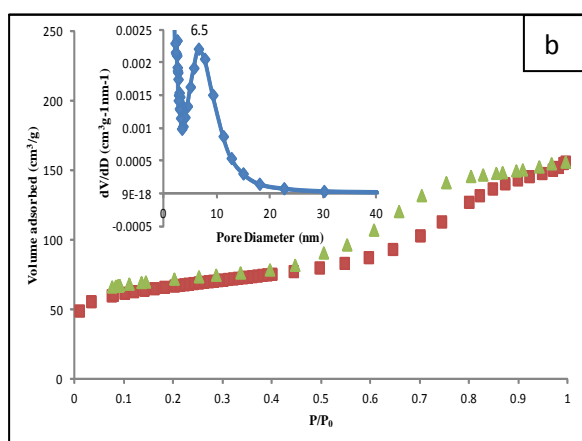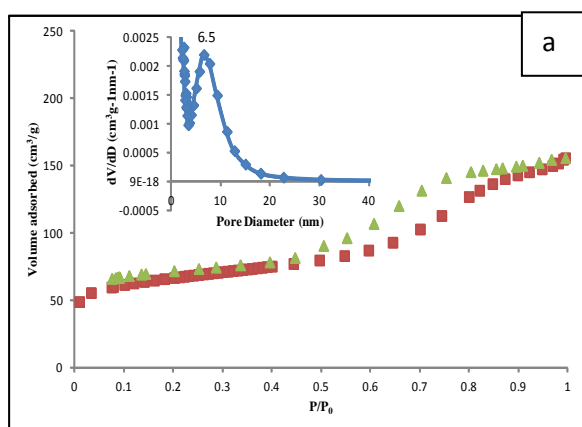
Figure 1

Photographs of the as-synthesized and the corresponding carbon monoliths are shown in Figures 1 a and b. 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 Figures 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. Figures 1 e and f show 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].

Figure 2(a) shows adsorption-desorption isotherm of the carbon monolith, which gave further insight into the porosity of the prepared material. A type-IV isotherm was obtained with hysteresis loop and a clear capillary condensation step at P/ ∼0.4-0.8 which is a characteristic exhibited by mesoporous materials [2]. It has a narrow pore size distribution centred at 6.5 nm calculated from the adsorption branch using the BJH method (insert) indicating uniform mesopore, with a surface area of 219 /g and a total pore volume of 0.21 /g. The pore system of the carbon monolith is almost exclusively mesopores, as it contains very few micropores from the t-plot analysis (Table 1).

The effect of different conditions on the synthesis was investigated by varying the ratio of the plant material to the pluronic F127, and time for the reaction. As the amount of the plant material used was increased to 5 g (ratio 1:2), the synthesised carbon monolith was still mesoporous and also has a narrow pore size distribution of 6.5 nm as shown in Figure 2(b), however the surface area reduced to 146 /g, which was due to the increase in the amount of plant material used to the template which is the pore forming component. An important criterion to use the template successfully is to adequately load the precursors into the porous network, which is normally carried out by an efficient impregnation of the solution within the pores of the template avoiding as much as possible only surface coating [16]. This was further confirmed when 7.5 g of the plant material was used (ratio 1:3); a non-porous carbon monolith was obtained. These

results show the possibility of changing easily the surface area, pore size distribution and pore volume of carbon monoliths, without necessarily changing the monolithic aspect and the macro-morphology, which could help in tailoring the porous structure to fit into specific application. The summary of the structural properties for the different ratios is given in Table 1. For the effect of time, when 24 and 48 hours were used, the synthesized carbon monolith cracked and when the time was more than 72 hours no significant difference was observed in the carbon monolith. In this study, the optimal reaction condition was found to be ratio 1:1 (template: plant material) and a reaction time of 72 hours. It should be noted here that the 72 hours preparation time used in this study is relatively long as compared to other evaporation-induced self-assembly and hydrothermal processes [1,6,15]. Our method, in contrast to other methods described in the literature, offers the benefit that no extra step is required for coating the scaffold, no heating is required to polymerize or evaporate the solvent and a cheap waste plant material is used as the carbon precursor. Therefore it is an interesting, and possibly an energy-efficient, and a cheaper alternative to other well established synthetic protocols.

Table 1

Figure 2

The XRD pattern of the carbon monoliths (Figure 3a) showed peaks representing different phases of graphite. The peaks at 2θ = 26.5º and 41º were indexed to (002) and (101) reflections of hexagonal graphite respectively (JCPDS No: 01-075-1621). In addition peaks at 29 º and 66.5º can also be seen which are probably due to an unknown impurity present in the waste plant material.
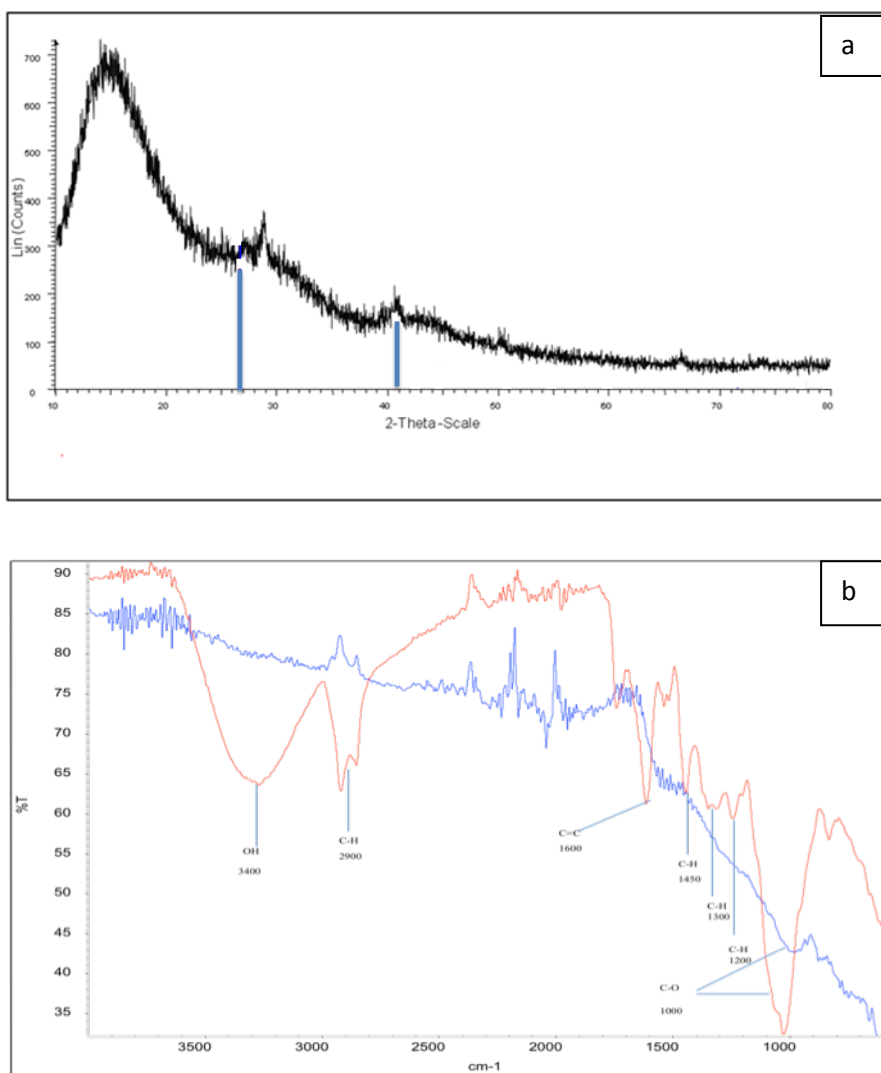

Figure 3

Figure 3(b) shows the FT-IR spectra of the as-synthesized (red) and the carbon monoliths (blue). The spectra have different shapes due to change in framework and high carbon content after carbonization. The determination of the main functional groups for a given wavelength is based on previous reports [6,17]. A broad band at about 3400 cm^{-1} is due to the –OH stretching of the phenolic groups in the as-synthesized

monolith. The peaks at about 1600 and between 1450-1200 cm^{-1} are due to the C=C stretching vibration of the aromatic and C-H bending vibration of aliphatic structures in the plant material respectively. The peaks at 2900 and 1000 cm^{-1} due to the C-H and C-O stretching vibrations of F127 respectively almost disappeared after carbonization confirming template decomposition. The peaks below 1000 cm^{-1} are due to aromatic C–H bending vibrations.

4. Conclusion

Mesoporous carbon monolith has been successfully prepared using triblock copolymer F127 as template and waste plant material as carbon precursor via an evaporation-induced self-assembly. The carbon monolith is crack-free, with high mechanical strength. In carbon science, materials of this nature are very promising, as they combine large pore volume with good mechanical stability. In comparison with other methods, this approach is simple and cheap, and the carbon monolith obtained could be applied in fields, such as, gas separation and adsorption, electrochemistry, and catalysis.

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Figure Captions

Figure 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 (f) SEM image of carbon monolith

Figure 2:   adsorption-desorption isotherm and pore size distribution of carbon monoliths (insert) (a) ratio 1:1 (b) 1:2 (F127:plant material)

Figure 3: (a) XRD pattern of carbon monolith (b) FT-IR of as-synthesized (Red) and carbon monolith (Blue)

Table

F127:plant material	Surface area (/g)	Pore size (nm)	Total pore volume (/g)	volume (/g)	volume (/g)
1:1	219	6.5	0.21	0.05	0.16
1:2	146	6.5	0.18	0.03	0.15
1:3	0.14	-	-	-	-

Table 1: Structural properties of the carbon monoliths

^a The micropore volume was calculated from the t-plot method.

mesopore volume is the difference between the total pore volume and the micropore volume.