**Microwave-assisted hydrothermal synthesis of carbon monolith via a soft-template method using resorcinol and formaldehyde as carbon precursor and pluronic F127 as template**

**Sunday E. Elaigwu\*, Georgios Kyriakou, Timothy J. Prior and Gillian M. Greenway**

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

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

**E-mail: s.e.elaigwu@2009.hull.ac.uk; sunnietrinex@hotmail.com**

**Abstract**

A new microwave-assisted hydrothermal synthesis of carbon monolith is reported in this work. The process uses microwave heating at 100 °C under acidic condition by employing a triblock copolymer F127 as the template, and resorcinol–formaldehyde as the carbon precursor. Scanning electron microscopy, Fourier transform infrared spectroscopy, nitrogen sorption measurements, transmission electron microscopy, X-ray studies and thermogravimetic analysis were used to characterize the synthesized material. The carbon monolith is crack-free, mesoporous and has a high surface area of 697 /g. The results demonstrate that the microwave-assisted hydrothermal synthesis is a fast and simple approach to obtain carbon monoliths, as it reduces effectively the synthesis time from hours to a few minutes which could be an advantage in the large scale production of the material.

**Keyword: Mesoporous Material, Microwave, Carbon Monolith, Hydrothermal**

## 1. Introduction

The preparation of carbon monoliths has been the subject of extensive research over the past two decades due to the number of applications these materials may find in the fields of catalysis, chemical separations, adsorption, chromatography, and as electrodes for electrochemical double-layer capacitors (EDLCs). In every case, the structural features and characteristics of the monoliths such as high surface area, thermal stability, and chemical inertness play a key role [1-5]. Nanocasting methods using mesoporous silicas as the "hard template" have been the traditional way of preparing these materials. However, the long processing time and the high cost of the synthetic protocol makes it difficult for the method to be employed for large scale manufacturing of these materials. An alternative way of forming carbon monoliths is the "soft-template" method, which involves the use of polymerizable precursor, such as,  resorcinol-formaldehyde [4,6], resorcinol-

phloroglucinol-formaldehyde [3, 5] or phenol-formaldehyde [7] as the carbon precursors, and amphiphilic block copolymer, usually F127 [3-6], cetyl trimethylammonium bromide (CTAB) [8], P123 [9], and mixed F127and P123 [7], as the pore-forming component. This method is more flexible and has been achieved using the conventional oven hydrothermal approach or the evaporation-induced self-assembly (EISA) methods [6]. The disadvantage of the above methodologies is that they are time consuming. Therefore, it is important to explore alternative time efficient methods for the preparation of carbon monoliths.

Microwave heating has been used in place of the conventional oven heating for preparing a variety of materials such as hydrothermal chars [10], inorganic nanomaterials, zeolites, ion-conductors and catalysts [11, 12]. The method is faster, cheaper and more energy efficient than the typical aqueous chemical processes [13]. Despite the advantages of microwave heating in materials synthesis, its use in the hydrothermal synthesis of mesoporous carbon monoliths using resorcinol and formaldehyde as carbon precursor and pluronic F127 as a template has not been explored yet. Here we report a new microwave-assisted hydrothermal synthesis method for the preparation of mesoporous carbon monoliths via a soft template approach. The method appears to be simple and much faster as compared to conventional oven hydrothermal methods commonly employed for the preparation of this material.

## 2. Materials and methods

**2.1 Materials:** Poly(ethylene oxide)-b-poly(propylene oxide)-b-poly(ethylene oxide) triblock copolymer Pluronic F127 () and resorcinol were purchased from Sigma Aldrich, UK, formaldehyde and ethanol were purchased from Fischer Scientific, UK, while 37 % HCl was purchased from Romil, UK.

**2.2 Methods:** The synthesis was carried out in a microwave oven (MARS, CEM, Milton Keynes, UK equipped with XP1500 digestion vessels, with a magnetron frequency of 2.45 GHz, and 1600 W at maximum power). The pressure was monitored in a reference vessel during the reaction using a pressure sensor, while the temperature was monitored using an infrared fibre optic sensor installed in a ceramic sleeve in the same vessel. The method by Liu *et al.* [6] using conventional oven heating was adopted with modification. In a typical synthesis, 2.5 g of pluronic F127 and 1.65 g of resorcinol were dissolved in a mixture of deionised water and ethanol (20 ml each). A colourless solution was obtained after stirring for about 15 min. 0.2 g of 37% hydrochloric acid was added and the resulting solution was stirred for 1 hr. 2.5 g of formaldehyde was then added to the solution dropwise. The reaction mixture was vigorously stirred for another 1 hr, poured into a microwave reaction vessel made of Teflon and placed in a microwave oven. The mixture was heated between 50-100 ºC in the microwave oven

which was set to ramp to a given temperature in 5 min and was held at the temperature for 5-20 min. The maximum pressure attained during the process was 0.32 MPa. The reaction system was allowed to cool down to room temperature and the resulting polymer monolith (before carbonization) was collected by filtration, washed several times with de-ionised water, poured into a mold and dried in a conventional oven at 50 ℃ for 12 hrs, and then 80 °C for 12 hrs. The polymer monolith was carbonized in a tubular furnace under nitrogen flow to obtain the carbon monolith (after carbonization). The carbonization temperatures used was 600 ℃ for 6 hrs and was attained using a heating rate of 5 ℃/min. The carbon monoliths were denoted as $_{-y}$, where x and y represent temperature (℃) and time (min) in the microwave oven respectively.

**2.3 Characterization:** Nitrogen sorption measurements were performed on a Micromeritics Tristar BET-surface area analyser, Fourier transform infrared (FT-IR) spectra were collected on a Thermoscientific Nicolet 380 FT-IR using KBr pellets of the solid samples. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images were obtained using a ZEISS EVO 60 and a JEOL-2010 microscope respectively. SAXS data were collected on a powdered sample contained within glass capillary using a MAR345 image plate diffractometer operating with Cu Kα radiation over an angular range of $1 \leq 2\theta / ° \leq 8$. Thermogravimetic analysis (TGA) data were collected under   atmosphere at a heating rate of $30$ ℃ $min^{-1}$ using a Mettler Toledo-TGA/DSC 1 instrument. X-ray diffraction (XRD) patterns were recorded on a Siemens D5000 powder diffractometer using a Cu Kα X-ray source.

**3. Results and discussion**

The mechanism for the formation of mesoporous carbon monoliths through organic-organic self-assembly involves the strong interactions between the reacting species [14]. Firstly, polymerization slowly occurs between the resorcinol and formaldehyde forming water-soluble oligomers with hydroxyl groups capable of interacting through hydrogen bonding with the polyethylene oxide (PEO) segments of the template [15]. Typically, the homogenous reaction mixture separates slowly into two layers: the upper layer is the solvent (ethanol and water), while the lower layer is the polymer/template. Under the microwave-assisted hydrothermal synthesis, temperature and pressure play important role in enhancing the interaction between resorcinol and the formaldehyde which makes the polymerization process faster and accelerates the phase separation. A polymer monolith with rigid mesostructure is obtained from the lower phase. The polymer monolith has increased tolerance to internal pressure during the drying and carbonization steps and therefore does not form macrocracks

due to structural shrinkage. The template decomposes on carbonization turning the polymer monolith to a carbon monolith leading to the formation of mesopores [6].

The effect of time and temperature on the synthesis was first studied. The results are summarised in Table 1. At 50 ℃ for 5-20 min, no phase separation was observed in the microwave vessel. This could be attributed to the low temperature and pressure generated which were insufficient to enhance the polymerization reaction [6]. At 75 ℃ for 5-20 min, a small amount of colloidal product was obtained. However upon drying it turned to a gel which attached to the walls of the mold and could not be removed for further study. This could be due to the formation of a poorly cross-linked resorcinol-formaldehyde polymer [1]. At 100 ℃ for 5-20 min rigid polymer monoliths were obtained with slight difference in the yield depending on the synthesis time. Most of the discussion will be focused on the highest yield product ( -20).

**Table 1: Structural properties of the different carbon monoliths synthesized at 100 °C**

| Carbon Monolith (100 °C) | Yield (%) | BET surface area (/g) | Pore size (nm) | Total pore volume (/g) | volume (/g) | volume (/g) |
|---|---|---|---|---|---|---|
| -20 | 55±0.50 | 697±36 | 6.4±0.0 | 0.85±0.12 | 0.14±0.08 | 0.71±0.04 |
| -15 | 54±1.05 | 665±28 | 6.5±0.1 | 0.75±0.05 | 0.14±0.10 | 0.61±0.15 |
| -10 | 51±0.75 | 646±42 | 7.7±0.5 | 0.67±0.05 | 0.15±0.02 | 0.52±0.07 |
| -5 | 47±2.33 | 630±35 | 7.7±0.3 | 0.58±0.03 | 0.13±0.03 | 0.45±0.06 |

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

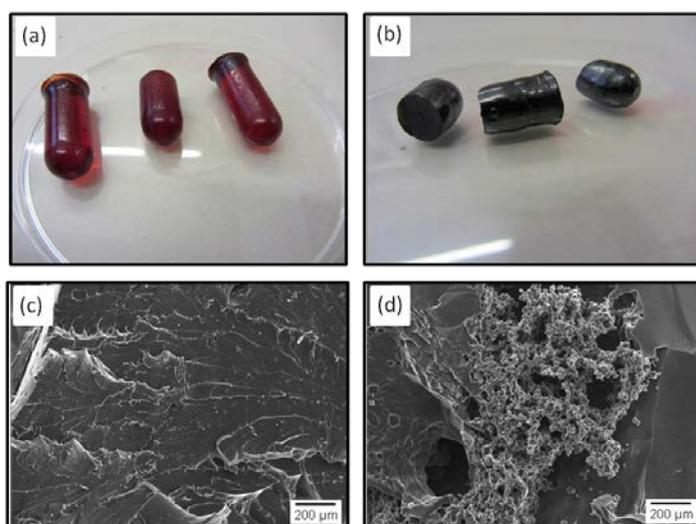mesopore volume is the difference between the total pore volume and the micropore volume.



**Figure 1:** (a) Photograph of polymer monolith (b) Photograph of carbon monolith (c) SEM image of polymer monolith (d) SEM image of carbon monolith.

Figure 1 (a) and (b) show photographs of the polymer monolith and the carbon monolith respectively. The polymer monolith displays a stable and crack-free bulk macroscopic appearance. The carbon monolith retained the same shape and macroscopic morphology and was also crack-free. However, the volume of the carbon monolith shrunk to about 50% as compared to the polymer monolith and the colour changed from orange to black. The SEM image of the polymer monolith shown in Figure 1 (c) suggests that the material was non-porous. Carbonization led to a porous carbon monolith with fused sphere-like microparticles of different sizes (10-20 µm) as shown in Figure 1 (d). The decomposition of the template during the carbonization process opened up the pores, and left the carbon precursor which formed the sphere-like microparticles and carbonaceous pore walls [3-5].
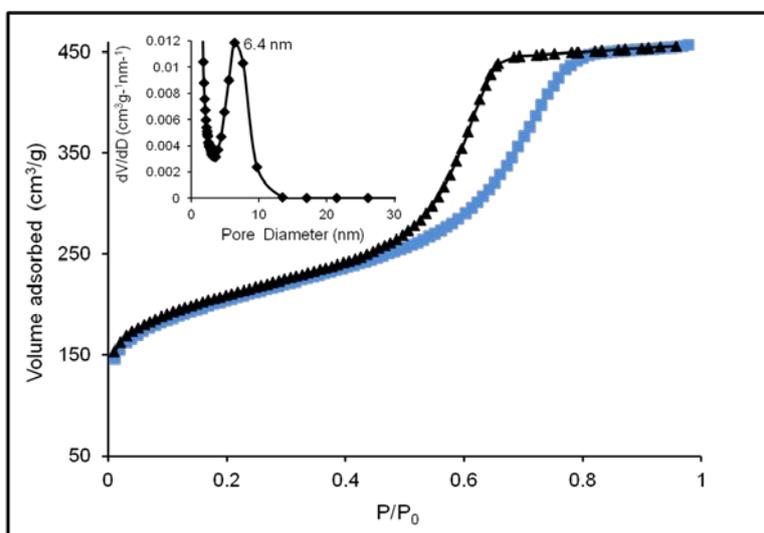


**Figure 2:** Nitrogen sorption isotherm and the pore size distribution for the carbon monolith.

The porous structure of the carbon monolith was investigated by the nitrogen sorption measurement (Figure 2). The summary of the pore structure for all the carbon monoliths is presented in Table 1. The carbon monolith showed a typical Type-IV isotherm with a hysteresis loop, and a clear step associated with the filling of mesopores due to capillary condensation at approximately P/ = 0.5–0.8. This suggests that the synthesized carbon monolith has uniform mesopores, with narrow pore size distribution of 6.4 nm and a BET surface area of 697 /g. The mesopores originate from the decomposition of the template. The increase in the amount of gas adsorbed at low relative pressure (P/ < 0.1) indicates the presence of micropores which could have originated from the generation of gases during the decomposition of the resorcinol-formaldehyde polymer [4]. The micropore volumes of the other carbon monoliths shown in Table 1 were very similar. In contrast, the mesopore volumes increase with increasing synthesis time in the microwave oven. $_{-20}$ synthesized at 100 ℃ for 20 min has

the highest BET surface area (697 /g) and pore volume (0.85 /g). The high surface area and the total pore volume data indicate that the carbon monoliths would exhibit excellent performance in applications, such as, adsorption, energy storage and catalysis [7, 16]. The results obtained in this study are consistent with previous reports using conventional oven heating [6, 7].

TEM was used to further characterise the polymer and carbon monoliths. The pore structure of the polymer monolith (not shown) was difficult to observe, due to the poor contrast between the resorcinol-formaldehyde polymer and the pluronic F127 template. However, carbonization of the material led to the opening of the pores due to the decomposition of the template and the condensation of the resorcinol-formaldehyde polymer skeleton [17] as shown in Figure 3(a). The mesopores in the carbon monolith were found to be approximately 6.0 nm which is in agreement with the result of the nitrogen sorption measurement. The XRD data for the carbon monolith is shown in Figure 3(b). The pattern depicts weak and broad diffraction features at about 27º and 43º which correspond to (002) and (101) reflections of graphitic frameworks respectively [2, 18]. The SAXS data shown in Figure 3(c) display a very broad feature around 2º suggestive of two broad peaks. These were assigned using a 2-D hexagonal lattice as the 10 (1.72º) and 11 (2.25º) peaks, corresponding to a hexagonal array with lattice parameter *ca*. 6 nm which is consistent with the pore size distribution observed by BET and TEM.  Each peak is very broad which suggests the sample is poorly crystalline on this length scale.  It is worth noting that resorcinol-formaldehyde polymer under acidic or basic conditions can form a rigid three dimensional network. Therefore, conventional polymerization will lead to cross linked polymeric networks instead of forming an ordered assemble around the micelle of the template [17].
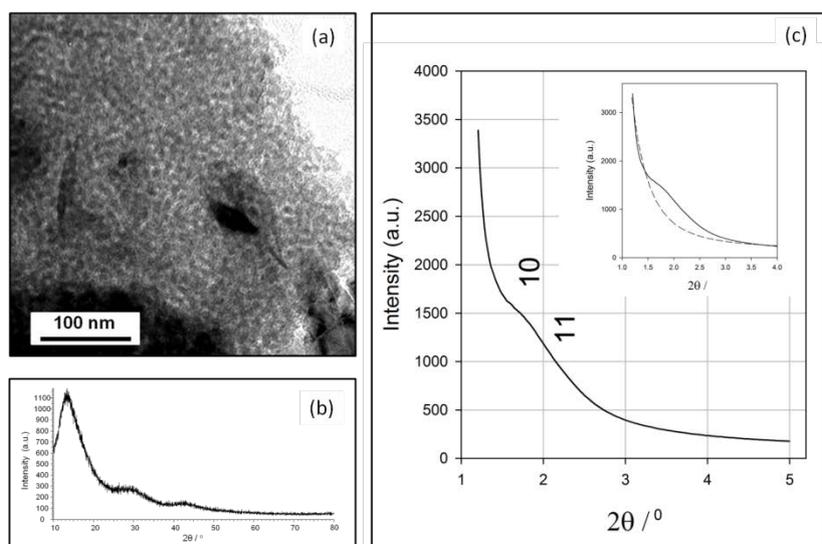


**Figure 3:** (a) TEM (b) XRD and (c) SAXS spectrum of the carbon monolith. The inset in (c) shows an expanded region of the data and highlights the broad feature in the data centred on .

Figure 4 (a) shows the FT-IR spectra of the polymer monoliths (red) and the corresponding carbon monolith (black), with different sections of the main functional groups being highlighted. The two spectra have different shapes, indicating a clear change in the framework. The assignment of the main functional groups is based on previous reports [1, 6]. A broad band present at about 3600-3000 cm$^{-1}$ (section 1) is due to –OH stretching, showing the presence of a large number of phenolic groups in the polymer monolith. The peaks at about 1600-1400 cm$^{-1}$ (section 3) assigned to the C-C stretching vibration of tri-substituted aromatic ring structure of phenolic resin framework of the resorcinol-formaldehyde polymer were retained after carbonization indicating the aromatic nature of the carbon monolith. The peaks at about 1200-950 (section 4) and 3000-2800 cm$^{-1}$ (section 2) assigned to the C-O and C-H stretching vibrations arising from the triblock copolymer F127 disappeared after carbonization of the material confirming the removal of the template. The peaks below 950 cm$^{-1}$ (section 5) are due to aromatic C-H bending vibrations. Figure 4 (b) shows TGA curves of the polymers (red) and carbon monoliths (black) under nitrogen flow. The TGA curve of the polymer monolith shows a sharp weight loss in the temperature range 300–400 °C. This is the typical temperature range were the decomposition of pluronic F127 occurs [5, 17] and confirms that the template successfully decomposed during the carbonization process at 600 °C, forming the mesopores in the carbon monolith.
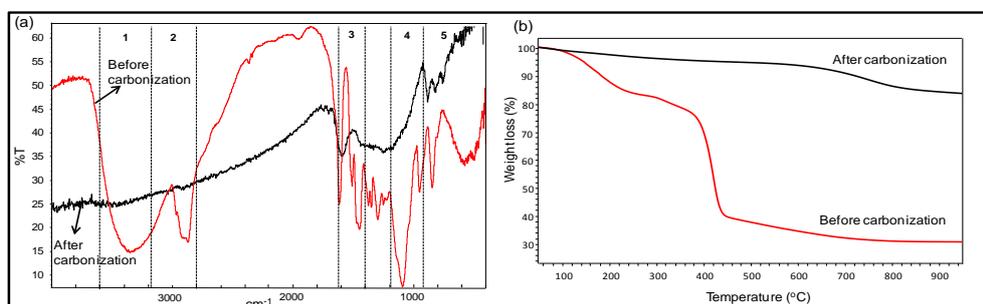


**Figure 4:** (a) FT-IR of polymer monolith (red) and carbon monolith (black) (b) TGA curves of the polymer monolith (red) and carbon monolith (black).

## 4. Conclusion

Mesoporous carbon monoliths have been successfully synthesized via a soft template approach using microwave heating. The synthesized carbon monolith was found to have uniform mesopores, with narrow pore size distribution of 6.4 nm and a BET surface area of 697 /g. The results obtained in this study demonstrate that the microwave-assisted hydrothermal synthesis is a fast and simple approach to obtain carbon monoliths within a very short time scale. The high yield of the carbon monolith obtained and the high speed of the microwave-assisted hydrothermal route suggest that the method could be of importance in the large-scale production of mesoporous carbon monoliths.

**Acknowledgement**

**References**

[1] Liu D, Lei JH, Guo LP, Deng KJ. Carbon 2011; 49: 2113-9.

[2] Elaigwu SE, Greenway GM. Mater Lett 2014; 115: 117-20.

[3] Tanaka S, Nakatani N, Doi A, Miyake Y. Carbon 2011; 49: 3184-9.

[4] Tanaka S, Nishiyama N, Egashira Y, Ueyama K. Chem Comm 2005; 2125-27.

[5] Tanaka S, Doi A, Nakatani N, Katayama Y, Miyake Y. Carbon. 2009; 47: 2688-98.

[6] Liu L, Wang FY, Shao GS, Yuan ZY. Carbon 2010; 48: 2089-99.

[7] Huang Y, Cai H, Feng D, Gu D, Deng Y, Tu B, et al. Chem Comm 2008; 2641-3.

[8] Li Z, Yan W, Dai S. Carbon 2004; 42: 767-70.

[9] Kim TW, Kleitz F, Paul B, Ryoo R. J Am Chem Soc 2005; 127: 7601-10.

[10] Guiotoku M, Rambo CR, Hansel FA, Magalhães WLE, Hotza D. Mater Lett 2009; 63: 2707-9.

[11] Cundy CS, Cox PA. Chem Rev 2003; 103: 663-702.

[12] Cushing BL, Kolesnichenko VL, O'Connor CJ. Chem Rev. 2004; 104: 3893-946.

[13] Nuchter M, Ondruschka B, Bonrath W, Gum A. Green Chem 2004; 6: 128-41.

[14] Liang C, Hong K, Guiochon GA, Mays JW, Dai S. Angew Chem Int Edit 2004; 43: 5785-9.

[15] Meng Y, Gu D, Zhang F, Shi Y, Yang H, Li Z, et al. Angew Chem 2005; 117: 7215-21.

[16] Huang CH, Doong R-A. Micropor Mesopor Mat 2012; 147: 47-52.

[17] Lu A, Spliethoff B, Schüth F. Chem Mater 2008; 20: 5314-19.

[18] Kim TW, Park IS, Ryoo R. Angew Chem 2003; 115: 4511-15.