



# Hierarchically porous carbon membranes containing designed nanochannel architectures obtained by pyrolysis of ion-track etched polyimide



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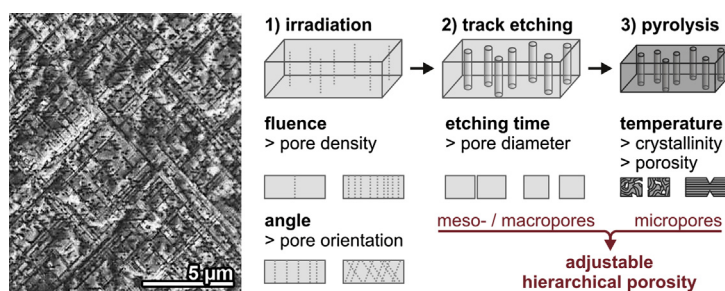
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## HIGHLIGHTS

- Pyrolysis of ion-track etched polyimide yields porous carbon membranes.
- Hierarchic porosity: continuous nanochannels embedded in a microporous carbon matrix.
- Freely adjustable meso- or macro-channel architecture introduced by ion-track etching.
- Channels give access to closed micropores: distinct increase of specific surface.
- High-temperature pyrolysis: graphitic carbon and pore closure due to crystallization.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

### Article history:

Received 8 April 2014

Received in revised form

6 August 2014

Accepted 2 September 2014

Available online 16 September 2014

### Keywords:

Microporous materials

Polymers

Etching

Heat treatment

Surface properties

## ABSTRACT

Well-defined, porous carbon monoliths are highly promising materials for electrochemical applications, separation, purification and catalysis. In this work, we present an approach allowing to transfer the remarkable degree of synthetic control given by the ion-track etching technology to the fabrication of carbon membranes with porosity structured on multiple length scales. The carbonization and pore formation processes were examined with Raman, Brunauer–Emmett–Teller (BET), scanning electron microscopy (SEM) and X-ray diffraction (XRD) measurements, while model experiments demonstrated the viability of the carbon membranes as catalyst support and pollutant adsorbent. Using ion-track etching, specifically designed, continuous channel-shaped pores were introduced into polyimide foils with precise control over channel diameter, orientation, density and interconnection. At a pyrolysis temperature of 950 °C, the artificially created channels shrunk in size, but their shape was preserved, while the polymer was transformed to microporous, amorphous carbon. Channel diameters ranging from ~10 to several 100 nm could be achieved. The channels also gave access to previously closed micropore volume. Substantial surface increase was realized, as it was shown by introducing a network consisting of  $1.4 \times 10^{10}$  channels per cm<sup>2</sup> of 30 nm diameter, which more than tripled the mass-normalized surface of

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the pyrolytic carbon from  $205 \text{ m}^2 \text{ g}^{-1}$  to  $732 \text{ m}^2 \text{ g}^{-1}$ . At a pyrolysis temperature of  $3000 \text{ }^\circ\text{C}$ , membranes consisting of highly ordered graphite were obtained. In this case, the channel shape was severely altered, resulting in a pronounced conical geometry in which the channel diameter quickly decreased with increasing distance to the membrane surface.

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## 1. Introduction

Synthesizing novel nanostructured carbon materials attracts great interest due to versatile applications including electrochemical capacitors, hydrogen storage, sensing devices and as support for heterogeneous catalysts [1–3]. So far, many synthetic routes for ordered and disordered porous carbon materials have been developed [4]. Where tunable and uniform pore sizes are required, template-methods are favored over direct synthetic approaches [5]. Different templates such as zeolites, mesoporous silica, nanoporous aluminum oxide, and synthetic opals have been used to create micro-, meso-, and macroporous carbon, respectively [6,7]. If functional templates such as metal oxide nanofibers are used which remain in the resulting material, this route also allows the fabrication of carbon composites [8].

Certain applications, such as heterogeneous catalysis, sensing or energy storage require carbon materials with a large and easily accessible surface. Considering effective molecular transport, the material's total surface area alone is not sufficient as a figure of merit [9]. Efficient mass transport of chemical species to and from the surface has to be taken into account as an additional, critical performance parameter. For these applications, meso- and macropores often enable better performance than micropores because of high mass transport rates, which are comparable to bulk values [10].

A major strategy to overcome performance drops caused by limited diffusion processes in microporous materials is the synthesis of hierarchically porous materials whose structure is optimized on multiple length scales [11]. As demonstrated for metals [12], silica [13], metal organic frameworks [14] and carbon materials such as monoliths [11], nanotubes [15] and spherical shells [16], a high surface area in conjunction with excellent molecular transport paths can be achieved by combining a microporous matrix with meso- or macropores. So far, only a limited number of hierarchically structured porous carbons have been synthesized. Possible routes are the pyrolysis of block copolymer-colloidal silica templates with successive carbon activation [17], templating of carbons using silica monoliths [11], chemical linking of carbon nanotubes with siloxanes leading to aerogels [18], and lithographic methods [19,20]. Also, a minor degree of mesoporosity could be introduced to microporous carbon derived from titanium carbide by altering the titanium extraction and annealing conditions [21].

These synthetic pathways show significant limitations in the pore size tunability. For instance, the dimension of the phase separation in block copolymers and the resolution of lithographic processes define the structure of the resulting carbons. It was demonstrated that these materials offer excellent functional properties such as high specific capacitances [11,22]. However, due to the limited tunability, the optimization of the pore structure remains restricted.

In this work, we present an efficient strategy for the synthesis of hierarchically structured porous carbon membranes featuring continuously organized meso- or macropore channels and channel networks inside a microporous carbon matrix. This was achieved by combining the pyrolysis of the char-forming polymer polyimide

[23] with the ion-track etching technique. The interaction of energetic ion beams in almost all polymeric matter creates latent damage tracks [24]. Controlled variation of the beam incidence direction can be used to fabricate a network of ion tracks [25]. Each projectile produces an individual track, thus the areal track density is adjusted by the number of ions which penetrate a substrate of given surface area [24,25]. In a second step, selective track etching creates channel-shaped pores and provides polymer membranes whose channel size and geometry can be widely tuned via the etching conditions [24]. Usually, ion-track etched polymer membranes are applied as templates for nanomaterial fabrication [25–29] or in fluidic applications [30], while our approach utilizes them as precursor material for subsequent carbonization. We will show that during pyrolysis, the specifically designed nanochannels within polyimide foils can be preserved, while the polymer matrix is transformed to microporous carbon, resulting in well-defined membranes of hierarchical porosity. Furthermore, we will demonstrate the flexibility of the outlined approach and evaluate the effect of the synthesis parameters on the morphology and the crystallinity of the resulting carbon membranes.

## 2. Experimental

### 2.1. Heavy-ion irradiation of polyimide foils

Kapton<sup>®</sup> HN type polyimide (from Du Pont<sup>™</sup> de Nemours) specimens with a size of approximately  $5 \times 30 \text{ mm}$  and a thickness of  $25 \text{ }\mu\text{m}$  were cut from commercial rolls. The size of the ribbons was chosen to fit into the quartz vessel used for the subsequent pyrolysis. Ion irradiation was performed at the linear heavy ion accelerator (UNILAC) at the GSI Helmholtz Centre of Heavy Ion Research using Au ions of about  $2 \text{ GeV}$  kinetic energy, and a projected range of about  $135 \text{ }\mu\text{m}$  in polyimide (calculated using the SRIM-2008 code [31]). For obtaining parallel channels, the polymer was irradiated perpendicular to the foil surface (fluence:  $2 \times 10^8 \text{ ions cm}^{-2}$ ), while for obtaining interconnected nanochannel networks, 4 irradiation steps were performed with an angle of impact of  $45^\circ$  to the surface normal. For each irradiation step, the angle was varied by  $90^\circ$  in the foil plane. Two samples with different fluences were prepared ( $2.8 \times 10^9 \text{ cm}^{-2}$  and  $1.4 \times 10^{10} \text{ cm}^{-2}$ ).

### 2.2. Ion-track etching and pyrolysis

The irradiated polyimide samples were etched with fresh NaOCl solution having 12% of active chlorine at  $70 \text{ }^\circ\text{C}$  for varying times to obtain channels of the desired diameter (etching rate:  $\sim 10 \text{ nm min}^{-1}$ ). Subsequently, the polymer membranes were pyrolyzed in a muffle furnace under high purity Argon 6.0 (99.9999%, Linde AG) atmosphere at  $950 \text{ }^\circ\text{C}$ . The temperature was increased with a heating rate of  $20 \text{ }^\circ\text{C min}^{-1}$ , and the final temperature was kept for 30 min followed by cooling to room temperature. For the high-temperature pyrolysis, the polymer sample was embedded within two graphite blocks and put in an Acheson oven. Heating to

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