Materials Letters 187 (2017) 56–59

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

Carbon nanocasting in ion-track etched polycarbonate membranes

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ARTICLE INFO

Keywords:
Ion beam technology
Carbon materials
Template synthesis
Pyrolysis
Nanowire networks

ABSTRACT

We replicate the unique pore structure of ion-track etched polymers with carbon using an organic sol-gel precursor strategy. First, phenol resin is cross-linked in the membrane pores, followed by selective dissolution of the template matrix and carbonization at a temperature of 550 °C. The potential to create nanomaterials of novel morphology is demonstrated by synthesizing free-standing, interconnected networks composed of aligned carbon nanowires of defined or modulated diameter.

1. Introduction

One-dimensional (1D) carbon structures such as nanotubes or nanowires (CNWs) represent one of the most important and frequently studied nanomaterial types. Due to their chemical, electrical, optical and mechanical properties, they can be employed in an exceptionally wide application range, including sensing, smart textiles, catalysis, battery technology or composite reinforcement [1–3]. One key challenge to improve the performance of such materials is to arrange them in ordered superstructures. By aligning 1D building blocks in e.g. fibers [1], arrays [2] or networks [3], their functionality, stability and handling can be enhanced. For instance, network architectures offer robustness, high surface area, continuous conduction and diffusion pathways and can be readily functionalized [3,4].

CNWs are almost exclusively synthesized by pyrolysis of organic precursor fibers [5,6] or by arc discharge [7]. The 1D polymeric precursor materials for these reactions can be prepared using electrospinning [6] or anisotropic structure formation during polymerization [5]. Also, it is possible to create nanowires from carbon nanotubes by amorphization [8]. The mentioned approaches only provide limited control over the dimension, aspect ratio, mutual orientation and interconnection of the CNWs. Additional reaction steps (such as lithographic processes and plasma treatments) can be used to modify the organic precursors [2], but the preparation of well-defined CNW superstructures remains challenging.

In this letter, we present a new strategy for the fabrication of CNW arrays. For the first time, we utilize the exceptional structural control provided by ion-track etched polymer templates in carbon nanocasting. These templates can be used to synthesize e.g. parallel arrays [9], networks or hierarchical assemblies [4] of 1D nano-objects. Conventional template-assisted carbon deposition routes require high-temperature processes such as chemical vapor deposition, and thus are limited to heat resistant templates such as anodized aluminum oxide [10], excluding ion-track etched polymers. To overcome this issue, we developed an organic precursor route which only requires moderate temperatures. To prove the synthetic value of the method, we created an interlaced CNW superstructure which cannot be accessed with existing techniques.

2. Materials and methods

2.1. Template fabrication and synthesis of resin solution

Three types of template membranes were produced from 30 µm thick polycarbonate foil (Makrofol). (i) A standard network template was created by irradiating the polymer foil from four directions with swift heavy ions (45° inclination to the template surface, 90° in-plane rotation after each irradiation, fluence=$0.7 \cdot 10^7$ ions cm^{-2} per step). Etching of the ion tracks was performed in NaOH solution (6M, 50 °C, 10 min), leading to the formation of a network of cylindrical pores of approximately 300 nm diameter. (ii) A network template with increased porosity was prepared as described above, but with doubled ion fluence. (iii) A template with only one parallel pore array was created by irradiating the polymer foil perpendicular to the surface (fluence =$1 \cdot 10^8$ ions cm^{-2}). In this case, the etching time was extended to yield a pore diameter of approximately 900 nm).

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http://dx.doi.org/10.1016/j.matlet.2016.10.040
Received 15 July 2016; Received in revised form 14 September 2016; Accepted 9 October 2016
Available online 11 October 2016

The standard resin for pore infiltration was prepared by polycondensation of phenol (0.6 g) and formaldehyde (2.1 mL, 37% in water) in alkaline solution (15 mL 0.1 M NaOH) for 0.5 h at 70 °C. A more concentrated resin composed of 10 mL 0.1 M NaOH, 2.0 g phenol, and 5.0 mL formaldehyde solution was prepared in an analogous manner. For details of the resin chemistry, the reader is referred to the literature [11].

2.2. Characterization

Thermogravimetric analysis (TGA) was performed using a STA 449C Jupiter (Netzsch, Germany) instrument in nitrogen atmosphere. Temperature programs for dynamic tests were run from 25 °C to 800 °C at a heating rate of 20 K/min. Scanning electron microscopy (SEM) was performed using a JSM-7401F microscope (JEOL) at 5–10 kV acceleration voltage. Transmission electron microscopy (TEM) was carried out with a CM20 (FEI, LaB_6 cathode) operated at 200 kV, using samples prepared by ultramicrotomy. The Raman measurement was performed using a microRaman HR800 spectrometer (laser wavelength: 514 nm).

3. Results and discussion

By etching out the ion tracks in polymers, membranes of tailored porosity can be produced [4]. Various polymers are suitable for ion-track etching and nanomaterial fabrication [4,9,12,13]. In this work, we chose polycarbonate as the template material based on two criteria: in contrast to other frequently employed polymers (e.g. polyimides or poly(ethylene terephthalate) [13]), it can be easily dissolved with commonly available solvents. Furthermore, it allows the fabrication of narrow pores of high aspect ratio without additional sensitization treatments, which can be required for e.g. poly(ethylene terephthalate) [13].

A scheme of the carbon nanocasting process can be found in Fig. 1. To prepare free-standing CNW networks, we used a template containing interconnected pore networks, which was obtained by selectively etching crossing ion-tracks in a polycarbonate foil with soda lye (Fig. 1, step 1). Subsequently, the pores were filled with an organic precursor by dipping the template into phenol resin solution (Fig. 1, step 2). After resin infiltration, the template membrane was dried at 80 °C for 10 min, and the process was repeated three times to ensure complete pore filling. Then, the resin was intensely cross-linked by heating the material to 150 °C for 30 min (Fig. 1, step 3). Contrary to the thermoplastic polycarbonate, the cross-linked resin cannot be dissolved in organic solvents, which allowed us to selectively remove the template matrix by washing the product with dichloromethane (Fig. 1, step 4). The as-obtained precursor material was subjected to pyrolysis, yielding a well-defined, self-supported network composed of aligned CNWs (Fig. 1, step 5). This structure reflects the morphology of the initial pore network, and can be considered inverse as compared to that of pyrolized and non-melting ion-track etched polymers [12].

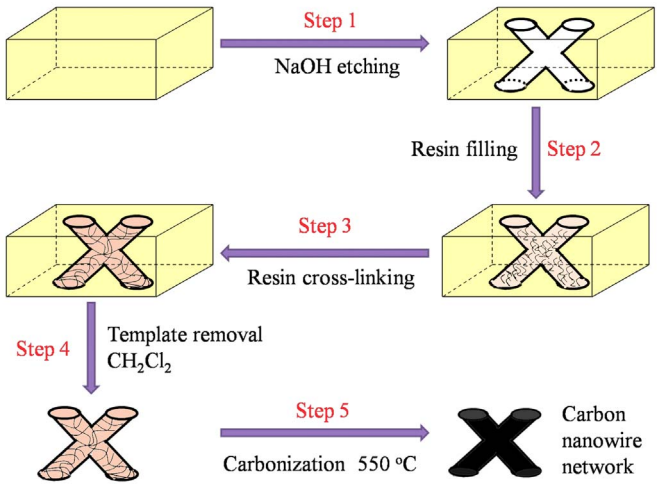

Fig. 1. Scheme of the carbon nanocasting process in polycarbonate templates.

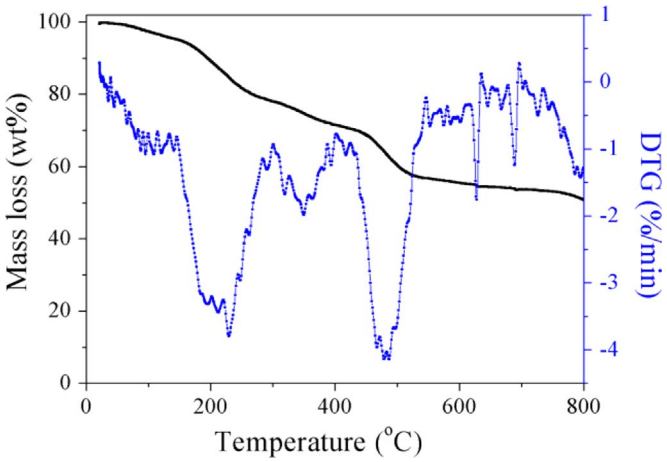

Fig. 2. Thermogravimetric analysis of the standard phenol resin.

The carbonization temperature chosen based on the thermogravimetric analysis of the resin (Fig. 2). Up to a temperature of 270 °C, a weight loss of 20% is found, corresponding to the evaporation of moisture and small molecules [14]. At higher temperatures, three overlapping pyrolysis regimes are observed, which are typically attributed to (i) the additional crosslinking of aromatic rings, (ii) the decomposition of the methylene groups and (iii) the release of aromatic hydrogen [14]. At 520 °C, a total weight loss of 42% is found, and a further temperature increase does not strongly affect the material. Accordingly, we selected 550 °C as the carbonization temperature for the CNW network (nitrogen atmosphere, hold time=2 h).

Electron micrographs of the product synthesized using the standard template are shown in Fig. 3. In the SEM survey image (Fig. 3a), the ordered network superstructure can be noticed. The material consists of aligned, uniformly distributed CNWs of similar diameter, whose orientation, density and thickness are defined by the porosity of the polycarbonate template. Due to the crossing and interconnection of the individual CNWs (Fig. 3b), a free-standing network is obtained. Transmission electron microscopy (TEM) was used to verify the formation of wires during the nanocasting process (Fig. 3c and d).

Two other membrane types were employed to evaluate the impact of the template fabrication conditions on the product morphology. By changing the ion fluence, the network density and connectivity can be controlled. As an example, we employed a network membrane with doubled ion fluence and thus pore density, which resulted in a more compact CNW superstructure (Fig. 3e). By changing the irradiation angle and the number of irradiation steps, the pore geometry can be defined. To test a template of differing pore architecture, we employed a membrane possessing one parallel array of pores, which are oriented perpendicular to the membrane surface. Ion-track membranes of this geometry are frequently applied in nanomaterial fabrication [9]. In the absence of crossing pores (and thus mutual stabilization of the therein deposited wires), bundles of carbon fibers were found after pyrolysis (Fig. 3f), which we ascribe to the aggregation of the resin wires during matrix removal and solvent evaporation. As the CNW diameter depends on the pore dimensions, it can be controlled by the etching step (e.g. it can be increased by extending the etching time, as shown in Fig. 3f).

The product morphology also depends on the resin chemistry. By infiltrating a standard network template with a phenolic resin of increased concentration, thicker CNWs with an undulated structure were obtained (Fig. 3g and h). Though a slight variation of the wire