

An optimized process for *in situ* formation of multi-walled carbon nanotubes in templated pores of polymer-derived silicon oxycarbide



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ABSTRACT

A reliable and optimized process to grow carbon nanotubes (CNTs) in templated pores of polymer derived ceramic (PDC) matrix was developed. It is realized through the pyrolysis of a preceramic polymer, i.e., poly (methyl-phenyl-silsesquioxane) (denoted as PMPS), in argon atmosphere at 1000 °C together with nickel-catalyst-coated poly-methyl-methacrylate (PMMA) microbeads (denoted as PMMA-Ni). PMPS served as both a precursor for the ceramic matrix and a carbon source for the CNT growth. PMMA microbeads were used as sacrificial pore formers and coated with nickel via an electroless plating method, which provides an improved control of particle size of the catalyst and its distribution in the material. The influence of PMMA-Ni loading on the *in situ* growth of CNTs and the properties of CNTs/SiOC nanocomposites were studied through thermogravimetric analysis (TGA), scanning electron microscopy (SEM), X-ray diffraction (XRD), Raman spectroscopy, and density/porosity measurements. Under optimized conditions, uniform distribution of *in situ* grown CNTs was observed within the templated pores of the SiOC matrix. The optimized process leads to reproducible high yield of CNTs in the pores. The development of such novel CNT/cellular ceramic nanocomposite materials is of significant interest for a variety of sensor applications.

1. Introduction

For nearly four decades, preceramic polymers have been used to fabricate advanced polymer-derived ceramics (PDCs) due to the tailorability of their molecular structures and ease of processing [1]. In particular, Si-based polymers have been shown to be promising. Polymers, such as polysiloxane, have been converted into various ceramic products and forms: ceramic foams [2], bulk composites [3], planar tapes [4] and engineering materials with high temperature and oxidative stability [5,6]. Typical PDCs can be either insulating, like SiOC and SiOCN ($\sigma_{dc}(RT)=10^{-14}-10^{-12}(\Omega\text{ cm})^{-1}$), or semiconducting, like SiC and SiCN ($\sigma_{dc}(RT)=10^{-4}-10^2(\Omega\text{ cm})^{-1}$) [1]. Functionalizing and enhancing the electrical conductivity of SiOC ceramic foams, for example, could not only make use of their good mechanical, physical and chemical properties, but also potentially lead to several new applications, such as regenerable adsorber components or regenerable diesel particulate traps [7].

Different researchers [8,9] have identified that the carbon content (graphite or graphene phase) and interconnectivity of the carbon network within PDCs could exert a major influence on their electrical properties. This is mainly determined by the carbon species (especially phenyl groups) in the starting polymer and processing methods, e.g., adding carbon-rich compounds, using special pyrolysis conditions. Alternatively, introducing carbon nanotubes (CNTs) into PDCs is expected to be an effective and promising method for further electrical property enhancement due to their high conductivity [10,11]. However, there are two handicaps that hinder the use of CNTs in PDCs as either functional or structural reinforcement: high manufacturing cost and non-uniform dispersion in matrix materials. To overcome these handicaps, *in situ* formation of CNTs can be achieved by utilizing the hydrocarbon species released in a large amount during the thermal transformation of polymer precursor to ceramic. With catalyst, these hydrocarbon species can be converted to CNTs in the intermediate temperature range and this process is a type of the so-called Catalyst

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Assisted Pyrolysis (CAP). In other words, CAP method could help turn waste gases into useful functional component: CNTs.

Significant progress has been made in the production of nanostructures through the CAP method. Aside from turbostratic carbon, it has been shown that various nanostructures (whiskers [12], nanotubes [13–15], and nanowires [16]) can be produced directly from preceramic polymers. For example, Vakifahmetoglu et al. [17] described the production of Si_3N_4 and SiC nanowires using poly(methyl-phenyl)silsesquioxane (PMPS) with a cobalt catalyst. Likewise, single-crystalline Si_3N_4 nanowires/nanobelts were produced from polysilazane, using FeCl_2 as catalyst [18]. Yang et al. reported SiC nanorods that were synthesized using a similar methodology [19]. More specific regarding carbon species through CAP, Greil et al. [20] showed that, in two types of polysiloxane derived Si-O-C ceramics, the precipitation of the amorphous carbon phase began with polymer decomposition, typically at 400 °C, and was nearly completed at 1000 °C. Above 1100 °C, the crystalline carbon species were found, which resulted in percolation of the electrically conductive network of turbostratic carbon. Scheffler et al. [21] observed for the first time the direct formation of multiwall carbon nanotubes (MWCNTs) only within the pores that formed during the polymer-to-ceramic conversion of PMPS which contained nickel acetate. These active pores were described as “catalytic microreactors”. Later, they showed the *in situ* growth of CNTs when nickel acetate and silicon were incorporated together into the PMPS precursor/silicon mixture [22]. In a related study, using polymeric microbeads as sacrificial pore formers, Terry et al. showed the formation of CNTs in these templated pores [23]. Furthermore, CNTs were synthesized from a borazine-based precursor including nickel catalyst [24] and Ya-Li Li reported the fabrication of SiOC-CNTs composite by a one-step process via the *in situ* growth of CNTs during the pyrolysis of a preceramic polymer (polysiloxane) including FeCl_3 as catalyst [25]. Recently, Mantzel et al. [26] took one step further to not only *in situ* form CNTs in pyrolyzed Si-O-C samples but also sinter/densify the ceramic body by field assisted sintering technology, and their results showed that CNTs could survive the harsh sintering conditions and significantly improve the mechanical properties, e.g., hardness, for the samples sintered at 1050 °C when compared with CNT-free ones.

In most of these studies, the nanotubes and whiskers form on the exposed surface of the sample or on the wall of pores in the matrix. However, due to lack of control over the location/distribution of the catalyst and the quality of catalyst carriers, e.g., microbeads as pore formers, the full efficiency of the process has not been realized. For instance, simply mixing catalyst compound with preceramic polymer would lead to the random distribution of catalyst particles in the ceramic matrix, thus only a portion of them that happens to be on the pore/crack surfaces would contribute to the CNT growth. Even if the catalyst compound is coated on the shell of pore formers, CNTs could only grow on catalyst seeds/particles of a limited range of sizes, which imposes another technical challenge to the processing - control of the thickness of catalyst shell. Finally, in many of the studies reported in the literature, some of the key details are lacking, making it hard to reproduce these results.

The present study focuses on a novel procedure for the *in situ* formation of CNTs inside templated pores of PMPS, aiming to

significantly improve the quantity and uniformity of the grown nanostructures. In addition, the processing is described with sufficient details. Nickel, as the transition metal catalyst, was uniformly coated on the surface of PMMA microbeads, denoted as PMMA-Ni, via an optimized electroless plating method. And then PMMA-Ni microbeads were added into PMPS polymer as the template porogen. By doing so, both catalyst particle distribution and porosity in the ceramic became well controllable, which in turn leads to a significantly higher yield of CNTs and more uniform distribution of the CNT network. These uniform composites are expected to have improved functional properties, including thermal and electrical conductivity.

2. Experimental procedure

2.1. Material processing

The ceramic matrix in this study was produced using the commercially available poly(methyl-phenyl-silsesquioxane) (PMPS, H44, Wacker Chemie AG, Burghausen, Germany). H44 is a solid polymer that has a good amount of carbon as methyl and phenyl groups, which serve as the major carbon source for MWCNT formation during H44 pyrolysis in an inert atmosphere. Poly-methyl-methacrylate (PMMA) microbeads (Microbeads AS, Skedsmokorset, Norway) with nominal size of 6 μm were coated with nickel shell in accordance with an electroless plating method described elsewhere [27]. These nickel coated PMMA microbeads, i.e., PMMA-Ni, were burned out during pyrolysis, leaving nickel nano-particles on the templated pore surfaces.

H44 and 0.5 wt% of aluminum acetylacetonate ($\text{Al}(\text{CH}_3\text{COCHCOCH}_3)_3$, the crosslinking agent) were completely dissolved in acetone (1 g H44: 1 ml acetone) first, then the PMMA-Ni microbeads prepared as mentioned above were gradually added into the solution with vigorous stirring. Different volume ratios of PMMA-Ni to H44 were used in the experiments (30:70, 40:60, 50:50, and 60:40). The mixture was stirred on a hot plate until the solvent partially evaporated, and was then transferred to an aluminum mold for crosslinking (4 h at 200 °C in air; heating rate: 5 °C/min). The cross-linked porous monolithic bodies were crushed into powder, then cold-pressed into pellets at room temperature. Samples of different compositions were pyrolyzed at 1000 °C with heating rate of 2 °C/min under ultrahigh purity argon (static, oxygen gettered) in a tube furnace, held for 1 h at peak temperature and finally cooled down at the rate of 3 °C/min. Based on the volume percentage of PMMA-Ni used (with respect to the starting materials), samples were labeled as SiOC-Ni30, SiOC-Ni40, SiOC-Ni50, SiOC-Ni60. The processing route is schematically illustrated in Fig. 1.

2.2. Characterization techniques

Thermogravimetric analysis was carried out in argon atmosphere up to 1200 °C (STA 409, Netzsch GmbH, Selb, Germany) with heating rate 2 °C/min. Three different types of samples were tested: pure H44, PMMA-Ni microbeads and cured PMMA-Ni/H44 (50:50 vol ratio).

The morphological analysis of fracture surfaces of the pyrolyzed samples was performed by scanning electron microscopy (SEM) (JSM-7000, JEOL, Tokyo, Japan) with an accelerating voltage of 10 keV.

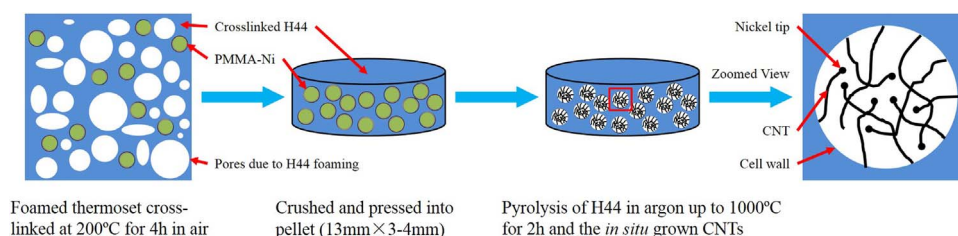


Fig. 1. Schematic for the *in situ* growth of carbon nanotubes in the templated porous SiOC ceramic (not to scale).

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