



Feature article

Preparation and characterization of polymer-derived Zr/Si/C multiphase ceramics and microspheres with electromagnetic wave absorbing capabilities



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ABSTRACT

Precursors for Zr/Si/C multiphase ceramics were synthesized by the reactions of dilithiozirconocene complex with dichlorodimethylsilane, methyltrichlorosilane and dichloromethylvinylsilane, respectively. The precursor-to-ceramic process of the precursor was investigated by TG-GC-MS and TG-FTIR analyses, confirming a complete transformation from organometallic polymers into ceramics below 800 °C. Annealing experiments of the derived ceramics at temperatures from 1000 °C to 2000 °C indicated the crystallization from ZrSiO₄, ZrO₂ to ZrC. Furthermore, micrometer-sized Zr/Si/C ceramic microspheres were successfully fabricated from the precursor at 1000 °C, showing surface morphology like wrinkled pea. According to the XRD, HRTEM and XPS analyses, such multiphase ceramic microspheres consist of ZrSiO₄, ZrO₂, and amorphous SiO_xC_y. Interestingly, the ceramic microspheres performed satisfactory electromagnetic wave absorbing capacity with the RL_{max} reaching -34 dB, which could be potential candidates for electromagnetic micro-devices.

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1. Introduction

Ceramic microspheres have promising practical applications in the field of catalyst support, adsorption, thermal insulation and so forth [1,2]. Compared with polymer microspheres, such ceramic microspheres usually perform superior thermal stability and better corrosion resistance, which have attracted much attention on their application in harsh environments. Nevertheless, the usual methods such as grinding, extrusion dripping or vibrational droplet coagulation always bring with drawbacks of poor sphericity and unfavorable uniformity, limiting the preparation of ceramic microspheres [3,4].

Polymer-derived method has generated widespread interest for their flexibility to manufacture ceramics with diverse shapes such as fibers, foams or micro beads [5–7]. By using polymeric precursor microspheres as the precursors, ceramic microspheres could be obtained after sintering at high temperature. Despite the suc-

cessful fabrication of various Si/C/N/Ni [8], Fe/Si/C [9], Ti/O/Si/C/N ceramic microspheres [10], the polymer-derived Zr/Si/C ceramic microspheres have not been reported yet. The Zr/Si/C-containing materials may turn into ultra-high temperature ceramics such as ZrC-SiC. With high melting points, high hardness and excellent chemical stability, such ultra-high temperature ceramics could bear temperatures over 3000 °C and therefore can promisingly be applied in various harsh environments [11].

In this paper, the preparation of polymer-derived Zr/Si/C multiphase ceramics is reported. Furthermore, pyrolysis of the precursor and crystallization behavior of the derived ceramics are investigated by combined characterization methods. Polymer-derived Zr/Si/C ceramic microspheres are successfully obtained from the precursor, which interestingly display electromagnetic wave absorbing performance.

2. Experimental procedures

2.1. Materials

Dichlorodimethylsilane (Me₂SiCl₂, 99%, CAS#75-78-5), methyltrichlorosilane (MeSiCl₃, 98%, CAS#75-79-6), dichloromethylvinylsilane (CH₂=CHSiCl₂, 97%, CAS#124-70-9), *n*-butyl lithium (*n*-BuLi, 2.4M in hexane, CAS#109-72-8) and *N,N,N',N'*-tetramethylethylenediamine (TMEDA, 99%,

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CAS#110-18-9) were all obtained from J&K Scientific Ltd. Bis(cyclopentadienyl)dimethyl zirconium (Cp_2ZrMe_2 , 98%, CAS#12636-72-5), and silicone oil (CAS#63148-62-9) were purchased from Acros Organics and Alfa Aesar Ltd., respectively. Hexane (AR, 97.0%, CAS#110-54-3), tetrahydrofuran (THF, AR, 99.0%, CAS#109-99-9) and *N,N*-dimethylformamide (DMF, AR, 99.5%, CAS#68-12-2) were supplied by Sinopharm Chemical Reagent Co., Ltd. The solvents were dehydrated and deoxygenated prior to use, while other reagents were acquired at the highest purity. All synthetic reactions were carried out either under the atmosphere of N_2 or within the glove box unless otherwise noted.

2.2. Measurements

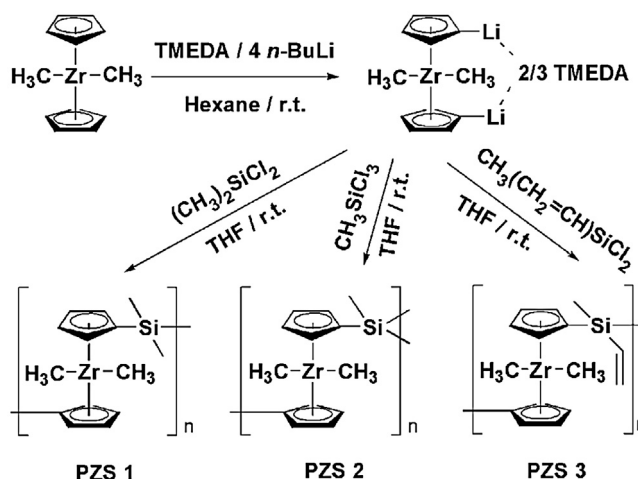
Fourier Transform Infrared (FT-IR, KBr pellet) spectra and Thermogravimetric-Fourier Transform Infrared (TG-FTIR) spectra were obtained using the FT-IR spectrometer (Frontier, Perkin Elmer, USA). Thermogravimetry-Gas Chromatography-Mass Spectrometry (TG-GC-MS, $50^\circ\text{C min}^{-1}$, under He), TG ($10^\circ\text{C min}^{-1}$, under N_2) and TG-FTIR ($50^\circ\text{C min}^{-1}$, under He) were investigated on thermogravimetric apparatus (Pyris 1 TGA, Perkin Elmer, USA). Mass Spectrograph (Clarus SQ8T, Perkin Elmer, USA) and Gas Chromatograph (Clarus 680, Perkin Elmer, USA) were used together for TG-GC-MS measurement as well. The morphologies, microstructures and elemental compositions of ceramics were observed by Field Emission Scanning Electron Microscope (FESEM, JEOL JMS-6700F, Japan) equipped with an Energy Dispersive Spectrometer (EDS, Oxford Inca, UK) and the High-Resolution Transmission Electron Microscope (HRTEM, FEI Titan G2 60-300, USA) with image corrector. Ceramic samples were directly used for the SEM observation, while polymer microspheres were gold sputtered for 60 s prior to the SEM measurement, in order to improve the electrical conductivity. X-Ray Diffraction (XRD) data were collected from 10° to 90° (2θ) on a diffractometer (D8 Advance, Bruker AXS, Germany), with $\text{Cu-K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) and a scanning step of 0.02° . X-ray Photoelectron Spectroscopy (XPS) measurement (Escalab 250Xi, Thermo Fisher Scientific, USA) were applied to analyze the elemental composition and chemical state. The electromagnetic wave absorbing capability of ceramics was measured on a network analyzer (8720ET, Agilent, USA) and evaluated according to reference.

2.3. Synthesis of preceramic polymers

Precursors named as PZS1, PZS2 and PZS3 were obtained by the polymerization between active dilithiozirconocene complex and Me_2SiCl_2 , MeSiCl_3 , $\text{CH}_2 = \text{CHSiCl}_2$, respectively. Specifically, 5.0 g Cp_2ZrMe_2 and 4.4 mL TMEDA were mixed with 80.0 mL hexane and stirred into suspension, followed by a dropwise addition of 20 mL *n*-BuLi (2.4 M hexane solution). After stirring over night (Ca. 10 h), the dilithiozirconocene complex (Zr-Li salt) was filtrated, purified with 3*30 mL hexane and dried under vacuum to give dry Zr-Li salt. 5.0 g of dry Zr-Li salt was well dissolved in 50 mL of THF, and a solution of 2.1 mL Me_2SiCl_2 (1.1 mL of MeSiCl_3 or 1.9 mL of $\text{CH}_2 = \text{CHSiCl}_2$) in 30 mL THF was added afterward. 12 h later, the reaction was terminated by 1.0 mL methanol, while lithium chloride was removed by filtration. Products were isolated by precipitation into hexane and subsequently dried under vacuum.

2.4. Preparation of polymer-derived ceramics

Pyrolysis of the precursor was conducted at heating rates programmed as Fig. S1 (Supporting information), to ensure a complete transformation from polymer to ceramics at 1000°C . Then the ceramic samples were sintered at 1200, 1400, 1600, 1800, 2000°C , respectively, with a heating rate of 4°C min^{-1} and a dwell time of 1 h. Corundum crucibles and quartz tube furnace were applied at



Scheme 1. Synthetic route of preceramic polymers.

target temperatures below 1200°C , while graphite crucibles and graphite furnace were used for target temperatures over 1200°C . A protective atmosphere of argon was maintained throughout all pyrolytic processes.

2.5. Fabrication of Zr/Si/C ceramic microspheres

0.4 g of Zr/Si/C polymer was dissolved and stirred in 1.6 g of DMF to prepare precursor solution (20 wt%). Simultaneously, 500 mL of silicone oil was heated (130°C) and stirred (300 r/min), prior to the dropwise addition of precursor solution. After heating and stirring for 4 h to remove the solvent (DMF), the self-assembled polymer microspheres solidified and gradually sank. Consequently, the upper emulsion was decanted while the polymer microspheres were collected, purified with hexane and dried under vacuum. Such microspheres were transferred for pyrolysis experiments, following the same sintering method explained in the pyrolysis of the precursor. Ceramic microspheres were then obtained for characterization and application.

3. Results and discussion

3.1. Preparation and pyrolysis of preceramic polymers

Three polymers containing Zr, Si and C were synthesized as illustrated in Scheme 1. The polymerizations of Me_2SiCl_2 , MeSiCl_3 or $\text{CH}_2 = \text{CHSiCl}_2$ were achieved separately, resulting in preceramic polymer PZS1, PZS2 and PZS3, correspondingly. The whole synthetic process was allowed to react at room temperature and highly repeatable. As can be identified from the FTIR spectra of precursors (Fig. S2, supporting information), peaks at 1252 cm^{-1} (Si- CH_3 stretching) and 797 cm^{-1} (Si-C and CH_3 vibration) together confirm the existence of Si- CH_3 [11]. The absorption at 2960 cm^{-1} can be attributed to the C-H vibration in $-\text{CH}_3$, while peaks at 977 cm^{-1} and 1464 cm^{-1} are assigned to the vibration of the C-H and C-C bonds of cyclopentadienyl (Cp) [12]. Peaks at 3100 cm^{-1} (unsaturated C-H of Cp ring) are overlapped by the huge peak of absorbed moisture (3430 cm^{-1}). The $-\text{C}=\text{C}-$ of Cp ring vibrates at 1640 cm^{-1} in all three precursors, while splitting peak ascribed to vinylsilyl in PZS3 can be observed at 1600 cm^{-1} .

As the temperature ascended, all of these preceramic polymers experience decreases in weight. As observed from the TG curves (Fig. 1), those organometallic polymers suffer noticeable decrease in weight below 200°C , possibly owing to the evaporation of the solvent and partial decomposition of the polymers [13]. Considerable weight loss occurs during the stage from 200°C to 450°C , after

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