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High-Temperature Nanoporous Ceramic Monolith Prepared from a Polymeric Bicontinuous Microemulsion Template

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Nonoxide ceramics are versatile materials with exceptional thermal and chemical stability and hardness. In particular, nanoporous[1] nonoxide ceramics are desirable for diverse applications such as catalysis, separations, water purification, and fuel cells.[2] Recently it has been shown that controlled nanoporosity can be achieved in such materials through a combination of self-assembly of amphiphilic molecules and decomposition of inorganic polymer precursors.[3−13] Although the synthesis of nonoxide ceramics with bicontinuous structure, that is, a continuous 3-D pore network, has been reported,[3−5] the pore sizes were ≤5 nm. Here, we describe the preparation of a novel nanoporous ceramic monolith with bicontinuous structure and 60−100 nm pores. The ceramic is obtained by a sequential process which replicates the structure of an all-hydrocarbon polymeric bicontinuous microemulsion (BμE).

There are several general approaches to the preparation of nanoporous ceramics from polymeric precursors. Self-assembled nanostructures of block polymers containing discrete inorganic and sacrificial organic blocks can be pyrolyzed to convert the respective domains to ceramic and pores.[7,8] Alternatively, organic block polymers can be designed such that inorganic homopolymers selectively partition into specific nanodomains; subsequent pyrolysis removes the organic framework and ceramizes the inorganic material.[9−13] The approach used here is to replicate the inverse structure of a rigid nanoporous template. The pores of the template are filled with a precursor melt which is then solidified and ceramized and the template selectively removed. This strategy is robust in that there is no need for controlled polymerization of inorganic monomers or careful design of block copolymer-precursor interactions. Moreover, it should be applicable to a wide range of precursors. Nanoporous nonoxide ceramics have already been prepared in an analogous manner using silica and carbon templates with ca. 2−5 nm pore sizes.[3−6]

To access significantly larger pores, we have derived a hard template from a polymeric BμE. This equilibrium, disordered phase comprising two interpenetrating networks with vanishing interfacial tension occurs in ternary blends of two chemically distinct homopolymers of equal size and the corresponding, symmetric diblock copolymer.[14−16] A single homogeneous phase is observed at high temperature, while upon cooling a composition channel of BμE separates a region of lamellar microphase separation at high copolymer content from a region of macro-phase separation at high homopolymer content.

The BμE employed consists of poly(ethylene) (PE), poly(ethylene-*alt*-propylene) (PEP), and poly(ethylene-*block*-ethylene-*alt*-propylene) (PE-PEP); the polymer synthesis and characterization are described in Supporting Information. Phase boundaries were determined through a combination of small angle neutron scattering (SANS), rheology, and transmission electron microscopy (TEM) (Supporting Information). A TEM micrograph of the BμE is shown in Figure 1a. Prior to imaging, the blend was rapidly quenched from the melt state to below the crystallization temperature of PE (~105 °C), which prevents disruption of the structure.[17] Contrast was obtained with RuO_4, a selective stain for PEP. A fit of the SANS scattering profile for this sample to the Teubner−Strey microemulsion model[18] indicates an average periodicity of 138 nm (Supporting Information).

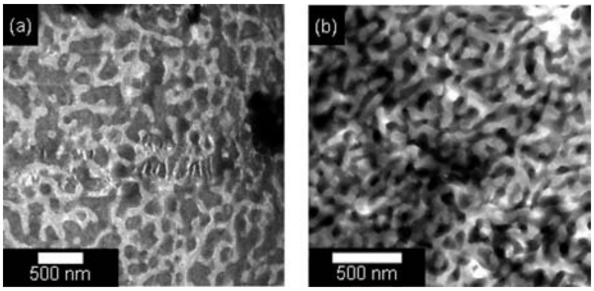

Figure 1. TEM micrographs of (a) PE/PEP BμE and (b) PE/C20 BμE-like composite made from solvent extraction of PEP and filling of pores with C20.

To obtain a nanoporous template, the melt morphology was first fixed by inducing PE crystallization through a liquid nitrogen quench. The resultant monolith (dimensions ca. 12 × 12 × 6 mm) was soaked in tetrahydrofuran (THF) at ambient temperature for several hours and then dried under vacuum. THF is a good solvent for PEP and a nonsolvent for PE. Weight measurements of the monolith before and after solvent extraction were consistent with the complete removal of PEP homopolymer. Note that no alignment step is needed in this procedure, owing to the isotropic, disordered nature of the BμE.

This nanoporous PE monolith was then used as a template for the synthesis of nanoporous SiCN. The ceramic precursor used is a commercially available polysilazane (Ceraset 20, C20), consisting of a silicon−nitrogen backbone with methyl and vinyl substituents.[19] Dicumyl peroxide was directly dissolved in the liquid C20 at 1 wt %. The monolith was then submerged in C20/peroxide solution under vacuum for ~24 h. Weight measurements indicate that this procedure is sufficient to fill the PE pores. The C20 was then cross-linked by heating to 90 °C for ~48 h to initiate decomposition of the peroxide. Cross-linking of the C20 prior to pyrolysis is essential to maximize ceramic yield and to maintain the nanostructure above the melting temperature of PE. A TEM micrograph of the resultant PE/C20 composite is shown in Figure 1b. The material is unstained; the contrast derives from the electron density difference between C and Si/N. Clearly, the structure of the BμE is preserved throughout the solvent extraction and pore filling procedures.

The PE/C20 composite was pyrolyzed under flowing N_2 at 1000 °C for 2 h, with heating and cooling rates of 2 °C/min. The ceramic

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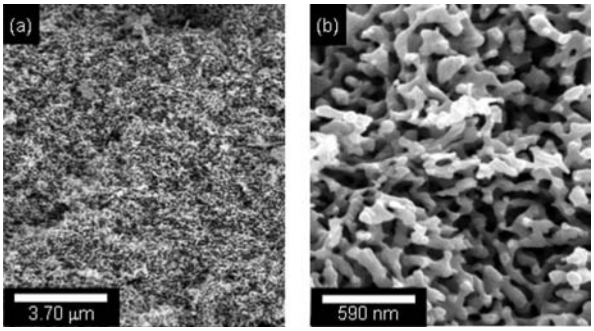

Figure 2. SEM micrographs of the nanoporous ceramic generated by pyrolysis of the BμE-like PE/C20 composite.

retained the shape of the original monolith during pyrolysis, with significant isotropic shrinkage (Supporting Information). Weight loss measurements were consistent with expectation under such conditions: 25% of the C20 and 100% of the PE. This indicates a significant advantage in the use of a polymeric material as a hard template over the silica and carbon templates.[3−6] In the latter case, the template must be removed by selective etching subsequent to pyrolysis; here, ceramic conversion and template removal are accomplished in a single step, owing to the thermal degradability of polymers. Despite the weight loss, shrinkage, and density increase associated with ceramization, the BμE structure is remarkably well-preserved, as evidenced by the scanning electron micrographs (SEM) presented in Figure 2. The micrographs clearly reveal a 3-D continuous pore structure with pores of well-defined size. This result is supported by nitrogen sorption measurements (Supporting Information). The pore size distribution, shown in Figure 3, was calculated using the Barrett−Joyner−Halenda approach.[20] Although the data points are sparse above 100 nm, the plot clearly corroborates a pore structure of well-defined size. The observed peak spans a pore diameter of approximately 60 to 100 nm, in surprisingly good agreement with half the SANS domain spacing of the original BμE. The specific surface area of the material, determined by the Brunauer−Emmett−Teller method,[21] is 24 m^2 g^{-1}. The ceramic is stable under both air and N_2 to at least 1000 °C, as indicated by thermogravimetric analysis (TGA) (Supporting Information). We anticipate that the ceramic is amorphous. Previously published work suggests that crystalline phases can be formed if the pyrolysis temperature were increased to 1500 °C.[22] However, this could potentially disrupt the pore structure of the material. Energy dispersive spectroscopy (EDS) (Supporting Information) indicates an atomic composition of 37% Si, 31% C, 14% N, and 18% O. Prior to the pore filling procedure, the C20 is handled under ambient conditions; the O present in the sample and the relatively low N content can be attributed to reaction of water with Si−N bonds.[11] Handling of the C20 under inert atmosphere should be sufficient to produce SiCN.

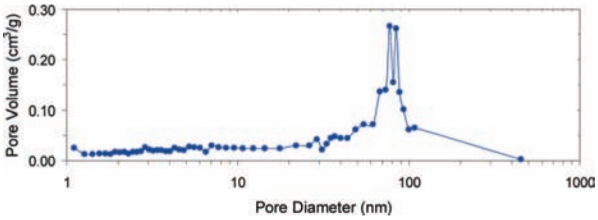

Figure 3. Pore size distribution of nanoporous ceramic calculated from desorption branch of nitrogen adsorption−desorption isotherm.

In summary, we have demonstrated the utility of polymeric BμEs for the production of nanoporous ceramics via hard template inverse replication techniques. The result is a pore structure entirely unprecedented in ceramic materials—disordered, 3-D continuous, and with a size range previously unattainable. The procedure is relatively simple and flexible and shows excellent preservation of the structure of the original polymer blend. This work should pave the way toward the production of nanoporous ceramics with tunable size and shape, via polymer blend and block copolymer templates. Furthermore, the technique described has the potential to allow for unique ceramic-containing composites.

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Supporting Information Available: Additional references; materials and characterization; phase diagram for PE/PEP/PE-PEP; SANS profile for BμE; digital images of monoliths; and TGA, EDS, and nitrogen sorption isotherm data for nanoporous ceramic. This material is available free of charge via the Internet at http://pubs.acs.org.

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