Inorganic polymer-derived hollow SiC and filled SiCN sphere assemblies from a 3DOM carbon template

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Three-dimensional long range ordered hollow SiC and filled SiCN sphere assemblies were prepared for the first time by embedding low molecular weight pre-ceramic polymers of polymethylsilane and polysilazane into sacrificial 3DOM carbon templates which were subsequently burned out in air after pyrolysis under a nitrogen atmosphere.

In the micro/nano-fabrication field, the sacrificial template method has been successfully applied to generate a variety of tailored structures such as nanotubes,[1] nanorods,[2] nanowires,[3] nanofibers[4] and filter membranes.[5] Various macroporous and mesoporous materials including carbon,[6,7] polymer,[8] metal,[9] ceramics[10,11] and composite phases[12] have also been developed by this method. In particular, hollow nanospheres with an empty core and no inter-connection, which are useful as capsules for releasing drugs and biomaterials, pigment stabilizers in paints, photonic materials, chemical and biological sensors and catalysts,[13] have been fabricated *via* the template route. However, it is our view that little attention has been paid to non-oxide ceramic sphere structures, which exhibit excellent stability at high temperatures, high pressures and in chemically harsh conditions. During this study, we successfully prepared ordered assemblies of hollow SiC nanospheres and filled SiCN nanospheres by infiltrating three-dimensional ordered macroporous (3DOM) carbon as a sacrificial template with low molecular weight pre-ceramic polymers.

As the original template, colloidal silica spheres of different sizes were synthesized first by using a sol–gel reaction and were naturally sedimented to produce close-packed templates.[11] The achieved silica templates were then vacuum infiltrated with an 80% divinylbenzene (DVB) carbon precursor solution containing a free radical initiator, azobisisobutyronitrile (AIBN) (DVB–AIBN molar ratio = 25).[14] The silica–polymer composites were cured at 70 °C overnight and carbonized at 900 °C for 7 h under an Ar atmosphere. 3DOM carbons with BET surface areas (pore volumes) of about 94 m^2 g^{-1} (0.12 cm^3 g^{-1}) to 300 m^2 g^{-1} (1.32 cm^3 g^{-1}), corresponding to pore diameters of 150–1000 nm, were obtained after dissolving the silica spheres in 48% aq. HF. In the subsequent infiltration process, a highly viscous SiC precursor of about 480 cP s at 19 °C, polymethylsilane (PMS, –[Si(H)(CH$_3$)]$_n$–, M$_n$ = 580), synthesized as described in our previous report,[15] was diluted to 25 wt% in THF to infiltrate the carbon template. However the low viscosity SiCN precursor of about 80 cP s at 19 °C, polysilazane (PSZ, –(HNCH$_3$SiC$_2$H$_3$)$_n$– (HNHSiCH$_3$)$_n$–, M$_n$ = 440), synthesized by a method reported elsewhere,[16] was used with no dilution. The carbon-precursor composites were cured at 160 °C for 6 h in N$_2$. They were then placed in a quartz tube furnace under a dry N$_2$ flow and heated at 1 °C min^{-1} to 300 °C for 3 h, then heated at 1 °C min^{-1} up to a pyrolyzing temperature of 1250 °C for 30 min. The produced carbon–ceramic composites were finally oxidized in air at 650 °C for one hour to obtain the inter-connected SiC and SiCN sphere assemblies.

Fig. 1(A) shows a representative SEM (LEO1455VP) image of a SiC sphere product. It was observed that the highly ordered SiC spheres were obtained from 3DOM carbon frameworks. The spheres partly expose the empty core through small holes on the shells. In addition, a TEM (EM912 Omega) image clearly shows a regular ordered array of hollow spheres with dense shells as shown in Fig. 1(B). We generally found that the morphology of SiC sphere products is wholly dependent on the characteristics of the sacrificial carbon templates and the polymer concentrations used. The dimensions of the SiC hollow spheres range from a 135–896 nm outer diameter with a shell thickness of 14–79 nm when a 25% concentration of polymer solution was infiltrated into various carbon templates, as is shown in Table 1. The achieved ceramic spheres showed a very low shrinkage of 9–15%, compared to the pore size of the carbon template. This differs from the 25–30% shrinkage of our 3DOM SiC prepared from a sacrificial silica array template,[11] which is due to the thermally stable carbon template prepared at 900 °C, which could sustain the infiltrated framework through a high temperature conversion from the polymer to the ceramic phase more reliably than the silica array. Moreover, this method allowed us to prepare specimens with structural integrity spanning centimetres. On the other hand, it should be noted that the polymer solution with a concentration lower than 15% produced low quality samples without dense walls, whereas a concentration higher than 70% reduced the efficiency of infiltration due to its higher viscosity. At this point, it is reasonable to interpret that the prepared hollow structure was formed due to adsorption of the polymer into the template walls as the solvent was evaporated. An analogous case occurred when a glassy carbon nanopillar was synthesized by infiltrating the alumina membrane with the resin precursor.[1]
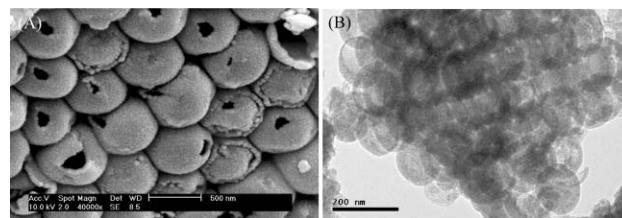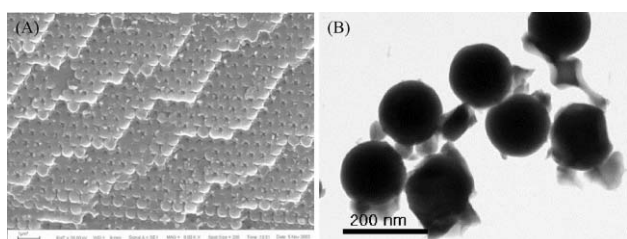

Fig. 1 The representative SEM (A) and TEM (B) images of 500 nm and 135 nm hollow SiC sphere assemblies, respectively.

When an undiluted low viscosity polysilazane was inserted into the carbon template, an ordered assembly of SiCN ceramic spheres with filled cores was produced, as shown by the SEM and TEM images in Fig. 2. Basically, the overall nanostructure was a replica of the original close packed silica spheres. The diameters of the 142–944 nm filled SiCN sphere nanostructures (shown in Table 1) were approximately proportional to the initial pore sizes, *ca.*

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150–1000 nm, of the sacrificial carbon templates used. The exceptionally low shrinkage of about 4–6% may be additionally due to pyrolytic circumstances in a confined space, where gaseous by-products formed during pyrolysis are re-deposited along the shrunken edges of polymeric structures. Besides, it is suggested that a slow heating rate below 600 °C, where major thermal decomposition occurred, stabilizes the ceramic structure by allowing gaseous products to be released gently in regions. The conversion chemistries of pre-ceramic polymers to SiC or SiCN ceramics are well documented.[16–18] However, it is surprising that homogeneously dense ceramic nanostructures can be obtained by a single infiltration of polymeric precursors. Eventually, additional evidence for the existence of a three-dimensional ordered structure in the assemblies was found. When small angle XRD (Bruker GADDS Germany) was measured for a hollow SiC sphere sample (500 nm dia.) and a filled SiCN sphere sample (142 nm dia.), a sharp peak was exhibited at 0.3° with 29.4 nm d-spacing, and at 0.54° with 16.3 nm d-spacing, respectively, which was consistent with the wall thickness of a burned carbon skeleton for each.

Fig. 2 The representative SEM (A) and TEM (B) images of 613 nm and 142 nm filled SiCN sphere assemblies, respectively.

Table 1 Characteristics of the achieved hollow SiC and filled SiCN sphere assemblies

	Hollow SiC sphere			Diameter of filled SiCN sphere/nm (Shr., %)
Pore size of porous carbon/nm	Outer diameter/nm (Shr.,[a]%)	Wall thickness/nm	BET As[a]/m² g⁻¹ (Vp[a]/cm³ g⁻¹)	
150	135(10)	14	50.8(0.265)	142(5.3)
200	173(13.5)	18	37.6(0.184)	—
350	317(9.4)	20	25.3(0.105)	334(4.6)
550	500(9.1)	38	19.3(0.074)	—
650	574(11.7)	50	10.8(0.061)	613(5.7)
750	640(14.7)	61	7.9(0.037)	—
1000	896(10.4)	79	5.0(0.038)	944(5.6)

[a] Shr.– shrinkage; A_s – surface area; V_p – total pore volume.

The thermal stabilities of the achieved SiC and SiCN spherical nanostructures were investigated in air up to 1000 °C (TA Instrument 2950) as shown in Fig. 3. It was surprising to find a significant difference in the thermal stabilities of the two types of PMS derived SiC products. The bulk SiC ceramic exhibited a final weight gain of 12% starting from 500 °C, whereas the hollow SiC spheres displayed almost no weight change even up to 1000 °C in air. The former behavior could be interpreted as being due to the oxidation of excess Si in the PMS derived SiC ceramic, as is well documented.[11,18] However, the latter behavior must be attributed to the beneficial role of the carbon template as a carbon source and to the formation of thermally stable stoichiometric SiC at 1250 °C. This explanation was confirmed by powder XRD (Siemens D5000, Cu Kα, radiation wavelength $\lambda = 0.154$ nm), which showed only three peaks at 36°, 61° and 72° (assigned to SiC (111), SiC (220) and SiC (311), respectively) with no Si peak.[18] Furthermore, it was found that both single peaks at −20 ppm in the ^{29}Si MAS-NMR spectra and at 22 ppm in the ^{13}C MAS-NMR spectra (600 MHz spectrometer, DSX600, Bruker) were explained by the presence of stoichiometric SiC, showing no free silicon or

carbon atoms.[18] In the case of the carbon-rich amorphous SiCN ceramic, which showed only a broad XRD peak at 15–40°, only a 5% weight loss was observed for the filled spherical nanostructure, whereas the bulk SiCN showed a weight loss of 12%, which might be attributed to advanced partial oxidation of the precursor-derived carbon when it was burned off.
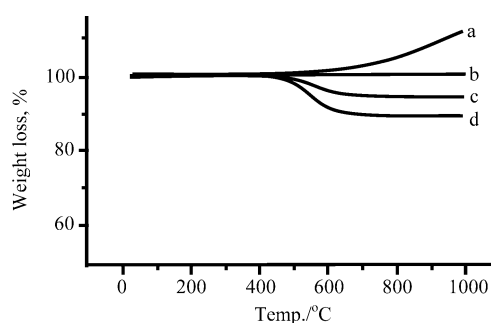
Fig. 3 Comparative thermal stability of the various ceramic products in air. (a) Bulk SiC from pure PMS, (b) hollow SiC sphere assembly, (c) filled SiCN sphere assembly and (d) bulk SiCN from pure PSZ.

Additional unique characteristics of the hollow SiC sphere assemblies were revealed by N_2 adsorption isotherms (ASAP 2400, Micromeritics). The BET surface areas are in the range of 5 to 50 m² g⁻¹, which are relatively low compared with the 94–300 m² g⁻¹ of porous carbon templates. However, it is worthwhile noting that the SiC pore structure showed outstanding high temperature stability with little change of surface area even after being exposed to air at 1000 °C for 0.5 h.

This work demonstrates the fabrication of ordered assemblies of hollow SiC and filled SiCN nanospheres, which can be tailored by controlling the sacrificial 3DOM carbon templates and the polymeric precursors. Moreover, the developed method appears to be well suited for the production of thermally and chemically stable non-oxide ceramics with unique spherical structures.

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