Anisotropic, biomorphic cellular Si₃N₄ ceramics with directional well-aligned nanowhisker arrays based on wood-mimetic architectures

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Abstract: Inspired by the transport behavior of water and ions through the aligned channels in trees, we demonstrate a facile, scalable approach for constructing biomorphic cellular Si₃N₄ ceramic frameworks with well-aligned nanowhisker arrays on the surface of directionally aligned microchannel alignments. Through a facile Y(NO₃)₃ solution infiltration into wood-derived carbon preforms and subsequent heat treatment, we can faultlessly duplicate the anisotropic wood architectures into free-standing bulk porous Si₃N₄ ceramics. Firstly, α-Si₃N₄ microchannels were synthesized on the surface of Cₚ templates via carbothermal reduction nitridation (CRN). And then, homogeneous distributed Y–Si–O–N liquid phase on the walls of microchannel facilitated the anisotropic β-Si₃N₄ grain growth to form nanowhisker arrays. The dense aligned microchannels with low-tortuosity enable excellent load carrying capacity and thermal conduction through the entire materials. As a result, the porous Si₃N₄ ceramics exhibited an outstanding thermal conductivity (TC, kR ≈ 6.26 W m⁻¹ K⁻¹), a superior flexural strength (σL ≈ 29.4 MPa), and a relative high anisotropic ratio of TC (kR/kL = 4.1). The orientation dependence of the microstructure–property relations may offer a promising perspective for the fabrication of multifunctional ceramics.

Keywords: silicon nitride; anisotropic; carbothermal reduction nitridation (CRN); wood; nanowhisker arrays

1 Introduction

Porous Si₃N₄ ceramics with a cellular structure, especially with unidirectionally aligned channels are promising candidates for hot gas or molten metal filtration, separation membranes, and catalyst carriers because of their excellent mechanical properties and gas permeability, high temperature stability, and outstanding thermal shock resistance [1–4]. Generally, these cellular ceramics are prepared by the sintering of the green body with unidirectionally aligned channels [5]. In the last decades, alginate gelation method [6,7] and freeze-drying [8–10] have been frequently used for the
preparation of the aforementioned green body. Unfortunately, a multitude of investigations on honeycomb Si₃N₄ ceramics exhibited less satisfactory permeability and mechanical properties, due to the heterogeneous architecture, loosely contacted grains on the cell wall of aligned channels, and relative low cell density. On the other hand, freeze-drying method through the unidirectional growth of ice has a high requirement for temperature and temperature gradient control [8–10]. The fabrication processes by self-organization method using an alginate template are complicate, expensive, and time-consuming. Ceramics that are ultralightweight, strong, and tough are in demand for a range of applications, requiring architectures and components carefully designed from the micrometer down to the nanometer scale. Biological materials can inspire new alloys to design sophisticated materials with intelligent and hierarchical microstructure [11–14]. Biotemplating technique, where natural grown structures are used as bulk templates for high-temperature conversion into ceramics, has attracted plenty of attention because of the unique biomorphic microstructures and high purity of the products.

Anisotropic structures are ubiquitous in biological materials. The structure of a tree features a large number of microchannels (i.e., lumina of tracheids, fibres, and vessels) along the longitudinal direction for mass (water, ions, and other components) transport. It has inspired the fabrication of hierarchically structured engineering ceramics [15–20]. Many kinds of wood-derived biomorphic ceramics such as TiC [18], Fe₂O₃ [19], Al₂O₃, TiO₂, and ZrO₂ [20] have been prepared by physical vapor infiltration-reaction (PVI-R) method, inorganic precursor–impregnation–calcination method, and sacrificial template method, respectively. However, high-performance wood-derived ceramics can only be achieved when the wood tissue is totally converted into the ceramic phase [21]. Vapor-phase infiltration by utilizing a solid–vapor reaction between the bio-carbon template and silicon-containing gaseous is an effective strategy for fabricating biomorphic wood-derived SiC ceramics with nanocrystalline structures [15,22–24].

Owing to the unique interlocking microstructure consisting of elongated β-Si₃N₄ grains, porous Si₃N₄ exhibits high strength and toughness. Silicon nitride powders have been synthesized by the carbothermal reduction nitridation (CRN) of rice husk-derived carbon and SiO₂ powder [25]. Luo et al. [26] have been fabricated wood-derived Si₃N₄ ceramics by the CRN reaction of wood-derived carbon infiltrated with Y₂O₃ and SiO₂ sol. Despite the imposing results reported for biomass-derived Si₃N₄ ceramics synthesized by the existing routes, some drawbacks still remain unaddressed. Unfortunately, degraded microstructure of the cell wall with Si-containing impurities or carbon always exists in the products due to the uncontrollable reaction [25,26]. Subsequently, the mechanical properties and reliability of the bulk ceramics are considerably deteriorated due to the degraded architecture compared with the original biomass microstructure. Besides degraded microstructure, complicate fabrication process is required for repetitious SiO₂ sol infiltration into wood-derived carbon preforms.

Herein, we demonstrate a facile, scalable approach for fabricating biomorphic cellular Si₃N₄ ceramics with directional microchannel alignments to reduce the tortuosity, for improving the thermal conductivity (TC) and the mechanical properties. Through the facile Y(NO₃)₃ solution infiltration and subsequent high temperature sintering, we can faultlessly duplicate the anisotropic wood tissue microstructure into free-standing bulk porous Si₃N₄ ceramics with devisable shape and size. The obtained biomorphic Si₃N₄ ceramics possessed peculiar hierarchical microstructure and anisotropic properties. In addition, the grain growth mechanism of directional β-Si₃N₄ nanowhisker arrays on the vertically aligned microchannels is investigated. The successful fabrication route, with its inner synergistic effect, offers an excellent approach to design and process advanced, strong, and integrated wood-like ceramics, which may have great potential applications in hot gas or molten metal filtration in the near future.

2 Experimental

2.1 Preparation of biomorphic cellular Si₃N₄ ceramics

Nature spruce woods were purchased from a furniture factory in Guizhou, China. SiO powders (particle size < 0.1 μm, Shanghai Aladdin Biochemical Technology Co., Ltd., China) were used as silicon source. The rectangular specimens in both the longitudinal (L) and radial (R) orientations with dimensions of 40 mm × 20 mm × 20 mm were cut from spruce woods which were fully naturally dried. Then, the specimens were dried at 110 °C for 24 h. The dried specimens were pyrolyzed at 1000 °C for 4 h under N₂ atmosphere with a low heating rate of 3 °C min⁻¹, resulting in a
porous bio-carbon template (C_B-template). The C_B-template was machined into blocks with dimensions of 20 mm × 4 mm × 3 mm and 10 mm × 10 mm × 3 mm in R- and L-directions, respectively. Subsequently, the C_B-templates were immersed in a 0.2 mol·L⁻¹ Y(NO₃)₃ solution for 4 h under vacuum condition. After drying and heat treatment at 1000 °C for 2 h, the C_B-templates attached with Y₂O₃ nanoparticles were obtained. Finally, the C_B-templates were put on a graphite plate with holes located in the gas outlet direction in the furnace (High Multi-5000, Fujidempa Co., Ltd., Osaka, Japan) and sintered at 1750 °C for 4 h under an N₂ pressure of 0.225 MPa. Silicon monoxide gas generated via sublimation of SiO powders, and reacted with the C_B-templates with and without Y₂O₃ to form bulk Si₃N₄ ceramics.

2.2 Characterization

The porosity and density were measured by the Archimedes’ method. Phase identification was performed by the X-ray diffractometer (X’Pert PRO, the Netherlands). Raman spectra were detected by the Thermo Scientific DXR Smart Raman spectrometer (Thermo Fisher DXR2xi, Thermo Fisher Scientific, USA). The morphology and quantitative elemental analyses of the bio-Si₃N₄ ceramics and the C_B-templates were performed by the scanning electron microscope (SEM, S-4800, Japan). The flexural strength was measured by a three-point bending method with a 16 mm span at an across-head speed of 0.5 mm·min⁻¹ at room temperature. Each final value was averaged over five measurements. The thermal diffusivity (α) and specific heat capacity (Cₚ) of specimens were measured by a laser-flash diffusivity instrument (Netzsch LFA467, Germany). The TC (k) of the Si₃N₄ samples was calculated according to the equation: 

\[ k = \rho \times \alpha \times C_p, \]

where \( \rho \) is the density of the specimens. Each final value was averaged over three measurements.

3 Results and discussion

Figures 1(a) and 1(b) display the optical photographs of the C_B-templates and cellular bio-Si₃N₄ ceramics. Although
pronounced linear shrinkage (23%–33%) occurs during the high temperature pyrolyzation processing (1000 °C), the macroscopic characteristics of spruce wood, such as the annual growth rings, are clearly visible in the biological carbon preforms (CB-templates). Comparing with the CB-templates, the bio-Si3N4 ceramics still retained the macroscopic bulk shape after sintering at 1750 °C for 4 h. No cracks and almost no shape changes are observed on the porous ceramics. The only observed change was a body-color transformation from black (the natural carbon color) to gray (the Si3N4 color), confirming that the CRN reaction occurred.

Figure 1(c) shows the XRD patterns of CB-templates and bio-Si3N4 ceramics. Amorphous carbon phase in CB-template is confirmed by the two broad diffraction bands at approximately 2θ = 23.9° and 43.98°. For the CB-template, after the SiO and N2 gas infiltration at 1750 °C for 4 h, primarily α-Si3N4 (No. 41-0360) and a trace of β-Si3N4 (No. 33-1160) phases were identified, which is also indicating the CRN reaction occurred according to the following reaction: 3SiO(g) + 3C(s) + 2N2(g) → Si3N4(s) + 3CO(g). The strong and sharp peaks indicate that the products have high crystallinity. Whereas, for the CB-template coating with Y2O3 additives, pure β-Si3N4 phase is achieved at the same sintering condition, indicating a phase transformation from α- to β-Si3N4 occurred through the dissolution–precipitation process in the Y–Si–O–N liquid phase [27]. The Y–Si–O–N secondary phase content is not detected, which may be due to the extremely low content. Except for the Si3N4, no other phase of silicon carbide (SiC), nor graphite, or other impurities were detected, indicating a high purity of the sintered products. It is noteworthy that SiC phase can be synthesized via the carbothermal reduction reaction between the SiO vapor and carbon materials. However, no SiC phase was found in the product in the present study.

In the SiO–C–N2 system, these following reactions may take place:

\[ 3\text{SiO}(g) + 3\text{C}(s) + 2\text{N}_2(g) = \text{Si}_3\text{N}_4(s) + 3\text{CO}(g), \]

\[ \Delta G_{\text{r}}^{\circ}(1) = -775,127 + 329,037 \text{J} \]

\[ 3\text{SiO}(g) + \text{C}O(g) + 2\text{N}_2(g) = \text{Si}_3\text{N}_4(s) + 3\text{CO}_2(g), \]

\[ \Delta G_{\text{r}}^{\circ}(1) = -1,292,396 + 856,097 \text{J} \]

\[ \text{SiO}(g) + 2\text{C}(g) = \text{Si}(s) + \text{CO}(g), \]

\[ \Delta G_{\text{r}}^{\circ}(1) = -83,345 + 8.797 \text{J} \]

where \( T \) is the sintering temperature.

Phase transformation from carbon to silicon nitride is most likely occurred in the SiO–C–N2 system rather than silicon carbide because \( \Delta G \) of Reaction (1) is lower than that of Reaction (3) at 1750 °C. Whereas, SiC would be preferentially formed as the sintering temperature is higher than 1900 °C.

As shown in Fig. 1(d), the peaks at about 1350 and 1580 cm\(^{-1}\) in the pyrolyzed CB-template are characteristic of the D (defect) and G (graphite) bands of graphitic carbon, respectively [28,29]. After the SiO gas and N2 infiltration, for the CB-template, the peaks of products at approximately 510, 560, 664, 763, 972, and 1032 cm\(^{-1}\) are observed, which are related to the lattice vibration of the α-Si3N4 crystal [30,31]. It is worth emphasizing that unreacted graphite phase is confirmed. Whereas, for the CB-template coating with Y2O3 additives, seven sharp peaks at approximately 446, 615, 727, 862, 925, 936, and 1043 cm\(^{-1}\) are obviously observed, which can be well indexed to the β-Si3N4 [32]. The absence of graphite peaks is attributed to the complete CRN reaction. The weight gain of Si3N4(R) and Si3N4(4L) ceramics fabricated by CB-template without Y2O3 additives are 192.4% and 127.3%, indicating unreacted carbon retained in the products are ~33.1% and 55.9%, respectively. Whereas, the CRN reaction ratios of Si3N4(R) and Si3N4(4L) ceramics fabricated by the CB-template with Y2O3 additives are 93.7% and 89.3%, respectively, indicating nearly full CRN reaction. The results indicated that the phase transformation from α- to β-Si3N4 through the dissolution–precipitation process facilitated the CRN reaction.

Figure 2 shows the SEM images of the CB-templates and the anisotropic bio-Si3N4 ceramics sintered at 1750 °C for 4 h. It is worth mentioning that although large shrinkage occurs, the unique anisotropic structures of nature wood are well preserved after high-temperature carbonization. As shown in Fig. 2(a), the pyrolyzed CB-template directly inherits the anisotropic structure of the natural wood. The diameters of the large and small lattice-shaped subunits are approximately 15–20 and 30–40 μm, respectively. Cross-sectional view shows a vertically carbon alignment with very thin channel walls of 2–3 μm, which is duplicated the sophisticated microstructure of the natural wood, in which the long channels that extend throughout the material for directional transportation of water and nutrient (Fig. 2(b)). After the CRN reaction, the as-obtained bio-Si3N4 (α phase) ceramics directly inherit the anisotropic structure of the CB-template, including lattice-like channels of 15–40 μm in size and very thin channel walls of 2–3 μm (Figs. 2(c) and 2(d)).
macropore distribution is similar to the CB-template, and equiaxed α-Si₃N₄ grains on the cell wall are observed. The above results indicate that the vapor–solid CRN reaction allows the intrinsic unique structure of wood, featuring multiple aligned channels (i.e., vessels and lumina), to be well retained [33]. The homogeneous vertically aligned long channels within the CB-template play a vital role in the inheritance of wood tissue honeycomb microstructure during the phase transformation from carbon to Si₃N₄. The long microchannels guarantee intimate contacts between the solid carbon and the SiO gaseous together with N₂ atmosphere, which leads to a spatially homogeneous phase transformation toward a perfect honeycomb structure.

For the CB-template coating with Y₂O₃ nanoparticles, the as-obtained β-Si₃N₄ ceramics after sintering at 1750 °C for 4 h also inherit the anisotropic microstructure of the CB-templates (Figs. 2(e) and 2(f)). Meanwhile, vertically well-aligned β-Si₃N₄ nanowhisker arrays are observed on the microchannel walls, indicating the phase transformation from α- to β-Si₃N₄ occurred during the liquid sintering.

Figure 3(a) displays the enlarged SEM image of β-Si₃N₄ nanowhisker arrays on the microchannel walls. The single crystalline β-Si₃N₄ nanofibers are uniformly aligned normal to the microchannel wall surface. The length of β-Si₃N₄ nanowires is less than 8 μm and their diameter is smaller than 700 nm. Conventional solution–precipitation route is an effective approach to grow β-Si₃N₄ whiskers [34]. For the confirmation of microstructural characteristics of bio-Si₃N₄ ceramics, EDS patterns of elemental mappings of bio-Si₃N₄ ceramic are
shown in Fig. 3(b). As shown in Fig. 3(b), the quantitative analysis exhibits that the average atomic ratio of Si/N is approximately 4:4 (1:1), and the atomic percentage of Si is slightly higher. It may be due to the formation of natural SiO₂ oxide layer on the bio-Si₃N₄ ceramic surface.

As shown in Fig. 4, the entire nucleation-growth of β-Si₃N₄ nanowhisker arrays consists of four steps: (1) Homogeneous distributed Y₂O₃ nanoparticles are attached to the wall surface of long carbon microchannel after heat treatment at 1000 °C. (2) Long carbon microchannels covered with equiaxed α-Si₃N₄ crystallines are synthesized according to the vapor–solid CRN reaction. Meanwhile, Y–Si–O–N liquid phase are formed on the site of Y₂O₃ nanoparticles during sintering. (3) Large amount of β-Si₃N₄ nuclei are formed on the site of Y–Si–O–N liquid phase during the phase transformation process from α- to β-Si₃N₄ through the dissolution–precipitation mechanism. The Y–Si–O–N liquid phase facilitates the anisotropic β-Si₃N₄ growth along [0001] direction to form one-dimensional nanowhiskers, following the crystal prolongation mechanism [35–37]. (4) The nanowhisker growth starts with the large scale nucleation on the wall surface and the clusters of nanowhiskers quickly develop at a high temperature of 1750 °C. As a result, vertically well-aligned β-Si₃N₄ nanowhisker arrays are successfully synthesized. As reaction proceeds, the cell walls gradually become thinner, and these β-Si₃N₄ nanowhisker clusters get densely packed, leading to the large scale nano-arrays.

Figure 5(a) shows the anisotropic flexural strength of wood-derived bio-Si₃N₄ ceramics sintered at 1750 °C for 4 h. In contrast to conventional and isotropic Si₃N₄ ceramics derived from powder mixtures, a distinct anisotropy of the mechanical properties in different loading directions can be found. For the β-Si₃N₄ ceramics via C₉ template attaching with Y₂O₃ additives, despite the porosity is similar, the flexural strength in the L-direction (σᵢ = 29.4 MPa, porosity = 66.5%) is considerably higher than that in the R-direction (σᵣ = 13.6 MPa, porosity = 65.6%). For the α-Si₃N₄ ceramics derived from pure C₉-template, the flexural strength in the L-direction (σᵢ = 5.34 MPa, porosity = 77.9%) is also higher than that in the R-direction (σᵣ = 1.79 MPa, porosity = 75.8%), as indicated in Fig. 5(a). The anisotropic cellular microstructure leads to a significant anisotropy of σ. The strength of β-Si₃N₄ ceramics is much higher than that of α-Si₃N₄ ceramics, which is due to the existence of unreacted carbon on the products. The strength of the Si₃N₄ channel walls and the skeleton of Si₃N₄ is largely governed by their defect distribution. When the loading direction is parallel to microchannels, large micropores (40 μm) would result in low strength. However, few defects exist on the microchannel surface, leading to improved strength as loading perpendicular to the microchannels. The strength in the present research is much higher than that of the bio-SiC ceramics prepared by sol infiltration and carbothermal reduction (1±0.25 MPa) [38]. Low test results can be attributed to high porosity.

![Fig. 4 Schematic illustration of β-Si₃N₄ nanowhisker array growth mechanism.](image-url)
in the cell walls caused by the volatilization of two-thirds of the carbon mass of the template [20]. Moreover, the defect size of the microchannel walls was confined, resulting in the strong skeleton of bio-Si$_3$N$_4$ that can withstand larger force without rupture. As a consequence, the bio-Si$_3$N$_4$ ceramics exhibit superior specific flexural strength. Figure 5(b) shows the stress–strain curves of wood-derived Si$_3$N$_4$ ceramics. Under all test conditions, the specimens finally fail in a typically brittle mode. Loading in the longitudinal direction causes stepwise cracking between individual microchannels, which leads to a jagged curve shape. In contrast, a single and clear maximum curve is obtained under radial loading.

Figure 6 shows the anisotropic TC of wood-derived bio-Si$_3$N$_4$ ceramics. The bio-Si$_3$N$_4$ ceramics also exhibit a distinct anisotropy of the TC. The TC value of the β-Si$_3$N$_4$ ceramics via C$_B$-template attaching with Y$_2$O$_3$ additives (6.26 W·m$^{-1}$·K$^{-1}$, porosity = 68.9%) is much higher than that of Si$_3$N$_4(L)$ ceramics (1.51 W·m$^{-1}$·K$^{-1}$, porosity = 73.8%). For the α-Si$_3$N$_4$ ceramics derived from pure C$_B$-template, the TC value in the R-direction (1.98 W·m$^{-1}$·K$^{-1}$, porosity = 79.9%) is also higher than that in the L-direction (0.39 W·m$^{-1}$·K$^{-1}$, porosity = 81.8%). Due to the long aligned microchannels in the longitudinal direction being parallel to the direction of heat flow, the heat propagates more effectively in the vertical direction. The TC of β-Si$_3$N$_4$ ceramics is much higher than that of α-Si$_3$N$_4$ ceramics, which is due to the existence of unreacted amorphous carbon in the products.

We compared the TC of the bio-Si$_3$N$_4$ ceramics with other porous silicon nitride ceramics prepared by other methods, such as freeze-drying method [39] and foaming method [40,41]. Although the porosity is similar (60%–80%), the TC of bio-Si$_3$N$_4$ is considerably higher than that of porous Si$_3$N$_4$ ceramics (0.08–0.1 W·m$^{-1}$·K$^{-1}$) by sol–gel and freeze drying [39]. It is mainly caused by the undesired thermal resistance between loosely contacted Si$_3$N$_4$ grains on the vertically aligned microchannels. In addition, the TC is much larger than that of Si$_3$N$_4$ ceramics prepared by the foaming method (2.427–3.154 W·m$^{-1}$·K$^{-1}$ at porosity of 83.32%–86.42%). In a word, for the Si$_3$N$_4$ ceramics with randomly distributed whiskers, the only thermal conductive road access is a tortuous route. However, for our wood-derived bio-Si$_3$N$_4$ ceramics, the unidirectionally aligned dense microchannels with low-tortuosity served as a thermal conductive “expressway” for the rapid transport of phonons throughout the rigid framework. As a result, a high TC of 6.26 W·m$^{-1}$·K$^{-1}$ in the R-direction could be achieved. A high anisotropic ratio of TC ($k_R/k_L$) of 4.1–5.0 in bio-Si$_3$N$_4$ ceramics could be achieved. Many applications can benefit from the excellent anisotropic thermal properties of the bio-Si$_3$N$_4$ ceramics.
ceramics. Based on the orientation of the bio-Si$_3$N$_4$ ceramics and their thermal boundary conditions, bio-Si$_3$N$_4$ ceramics can be used in either thermal insulation or dissipation applications.

4 Conclusions

Biomorphic cellular Si$_3$N$_4$ ceramics with well-aligned nanowhisker arrays on the wall surface of directionally aligned microchannels were successfully fabricated by CRN and subsequent liquid phase sintering. Firstly, through a facile Y(NO$_3$)$_3$ solution infiltration into wood-derived C$_B$-templates and subsequent CRN reaction, long microchannels formed by equiaxed α-Si$_3$N$_4$ crystalline coating with Y$_2$O$_3$ nanoparticles were formed on the surface of C$_B$-templates. And then, Y–Si–O–N liquid phase on the cell walls of microchannels facilitated the anisotropic β-Si$_3$N$_4$ grain growth along [0001] direction to form nanowhisker arrays at 1750 °C. The directionally aligned dense microchannels enable excellent load carrying capacity and thermal conduction through the entire materials. As a result, the porous Si$_3$N$_4$ ceramics exhibited an outstanding TC ($k_R = 6.26$ W m$^{-1}$ K$^{-1}$), a superior flexural strength ($\sigma_f = 29.4$ MPa), and a relative high anisotropic ratio of TC ($k_R/k_L = 4.1–5.0$). The orientation dependence of the microstructure–property relation may offer a promising perspective for the fabrication of multifunctional ceramics.

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References

[1] Zhou Y, Hyuga H, Kusano D, et al. A tough silicon nitride ceramic with high thermal conductivity. Adv Mater 2011, 23: 4563–4567.
[2] Zhang Y, Yao DX, Zuo KH, et al. A novel route for the fabrication of porous Si$_3$N$_4$ ceramics with unidirectionally aligned channels. Mater Lett 2020, 276: 128264.
[3] Zhi Q, Wang B, Zhao S, et al. Simultaneous improvement in porosity and strength of porous β-Si$_3$N$_4$ ceramics by formation of ultrafine fibrous grains. Ceram Int 2021, 47: 8113–8122.
[4] Wang B, Yang J, Guo R, et al. Microstructure characterization of hot-pressed β-silicon nitride containing β-Si$_3$N$_4$ seeds. Mater Charact 2009, 60: 894–899.
[5] Riley FL. Silicon nitride and related materials. J Am Ceram Soc 2000, 83: 245–265.
[6] Ma N, Du LJ, Liu WT, et al. Preparation of porous Si$_3$N$_4$ ceramics with unidirectionally aligned channels. Ceram Int 2016, 42: 9145–9151.
[7] Thumbs J, Kohler HH. Capillaries in alginate gel as an example of dissipative structure formation. Chem Phys 1996, 208: 9–24.
[8] Liu RP, Yuan J, Wang CA. A novel way to fabricate tubular porous mullite membrane supports by TBA-based freezing casting method. J Eur Ceram Soc 2013, 33: 3249–3256.
[9] Liu RP, Xu TT, Wang CA. A review of fabrication strategies and applications of porous ceramics prepared by freeze-casting method. Ceram Int 2016, 42: 2907–2925.
[10] Wei ZL, Xie WQ, Zhang XY, et al. Preparation of AIN micro-honeycombs with high permeability via freeze-casting. J Eur Ceram Soc 2020, 40: 4462–4468.
[11] Schnep Z, Yang W, Antonietti M, et al. Biotemplating of metal carbide microstructures: The magnetic leaf. Angew Chem Int Ed 2010, 49: 6564–6566.
[12] Galusha JW, Jorgensen MR, Bartl MH. Diamond-structured titania photonic-bandgap crystals from biological templates. Adv Mater 2010, 22: 107–110.
[13] Yao H, Zheng G, Li W, et al. Crab shells as sustainable templates from nature for nanostructured battery electrodes. Nano Lett 2013, 13: 3385–3390.
[14] Huebsch N, Mooney DJ. Inspiration and application in the evolution of biomaterials. Nature 2009, 462: 426–432.
[15] Streitwieser DA, Popovska N, Gerhard H, et al. Application of the chemical vapor infiltration and reaction (CVI-R) technique for the preparation of highly porous biomorphic SiC ceramics derived from paper. J Eur Ceram Soc 2005, 25: 817–828.
[16] Pan JM, Pan JF, Cheng XN, et al. Synthesis of hierarchical porous silicon oxycarbide ceramics from preceramic polymer and wood biomass composites. J Eur Ceram Soc 2014, 34: 249–256.
[17] Chen CJ, Zhang Y, Li YJ, et al. Highly conductive, lightweight, low-tortuosity carbon frameworks as ultrathick 3D current collectors. Adv Energy Mater 2017, 7: 1700595.
[18] Yu M, Li GQ, Saunders T. Biomorphic wood-derived titanium carbides prepared by physical vapor infiltration-reaction synthesis. Ceram Int 2021, 47: 11459–11464.
[19] Liu ZT, Fan TX, Zhang W, et al. The synthesis of hierarchical porous iron oxide with wood templates. Micropor Mesopor Mater 2005, 85: 82–88.
[20] Cao J, Rambo CR, Sieber H. Manufacturing of microcellular, biomorphous oxide ceramics from native pine wood. Ceram Int 2004, 30: 1967–1970.
[21] Rambo CR, Sieber H. Novel synthetic route to biomorphic Al2O3 ceramics. Adv Mater 2005, 17: 1088–1091.

[22] Vogli E, Mukerji J, Hoffman C, et al. Conversion of oak to cellular silicon carbide ceramic by gas-phase reaction with silicon monoxide. J Am Ceram Soc 2001, 84: 1236–1240.

[23] Vogli E, Sieber H, Greil P. Biomorphic SiC-ceramic prepared by Si-vapor phase infiltration of wood. J Eur Ceram Soc 2002, 22: 2663–2668.

[24] Zhang JF, Zhou XN, Huang X, et al. Biomorphic cellular silicon carbide nanocrystal-based ceramics derived from wood for use as thermally stable and lightweight structural materials. ACS Appl Nano Mater 2019, 2: 7051–7060.

[25] Real C, Alcalá MD, Criado JM. Synthesis of silicon nitride from carbothermal reduction of rice husks by the constant-rate-thermal-analysis (CRTA) method. J Am Ceram Soc 2004, 87: 75–78.

[26] Luo M, Gao JQ, Yang JF, et al. Biomorphic silicon nitride ceramics with fibrous morphology prepared by sol infiltration and reduction–nitridation. J Am Ceram Soc 2007, 90: 4036–4039.

[27] Long ML, Li Y, Jin XM, et al. Silicon nitridation mechanism in reaction-bonded Si3N4–SiC and Si3N4-bonded ferrosilicon nitride. J Am Ceram Soc 2018, 101: 4350–4356.

[28] Deldicque D, Rouzaud JN, Velde B. A Raman–HRTEM study of the carbonization of wood: A new Raman-based paleothermometer dedicated to archaeometry. Carbon 2016, 102: 319–329.

[29] Paris O, Zollfrank C, Zickler GA. Decomposition and carbonisation of wood biopolymers—A microstructural study of softwood pyrolysis. Carbon 2005, 43: 53–66.

[30] Lukianova OA, Parkhomenko AA, Krasilnikov VV, et al. New method of free silicon determination in pressureless sintered silicon nitride by Raman spectroscopy and XRD. Ceram Int 2019, 45: 14338–14346.

[31] Xie T, Ye M, Wu YC, et al. Fourier transform infrared spectroscopy and Raman spectrum analyses of monocrystalline α-Si3N4 nanowires. J Chin Ceram Soc 2008, 36: 44–48, 53. (in Chinese)

[32] Sergo V, Pezzotti G, Katagiri G, et al. Stress dependence of the Raman spectrum of β-silicon nitride. J Am Ceram Soc 1996, 79: 781–784.

[33] Chen C, Hu L. Nanocellulose toward advanced energy storage devices: Structure and electrochemistry. Acc Chem Res 2018, 51: 3154–3165.

[34] Wang B, Xu ZY, Jin F, et al. Synthesis of rod-like β-Si3N4 seed crystals with tailored morphology. Ceram Int 2015, 41: 5348–5354.

[35] Björklund H, Falk LKL, Rundgren K, et al. β-Si3N4 grain growth, part I: Effect of metal oxide sintering additives. J Eur Ceram Soc 1997, 17: 1285–1299.

[36] Björklund H, Falk LKL. β-Si3N4 grain growth, part II: Intergranular glass chemistry. J Eur Ceram Soc 1997, 17: 1301–1308.

[37] Ren Z, Guo YB, Gao PX. Nano-array based monolithic catalysts: Concept, rational materials design and tunable catalytic performance. Catal Today 2015, 258: 441–453.

[38] Herzog A, Klingner R, Vogt U, et al. Wood-derived porous SiC ceramics by sol infiltration and carbothermal reduction. J Am Ceram Soc 2004, 87: 784–793.

[39] Zhao XT, Wang HL, Shang W, et al. Properties and processing of porous Si3N4 ceramics. Key Eng Mater 2014, 602–603: 375–379.

[40] Yin LY, Zhou XG, Yu JS, et al. Highly porous silicon nitride foam prepared using a route similar to the making of aerated food. Int J Appl Ceram Technol 2016, 13: 395–404.

[41] Yin LY, Zhou XG, Yu JS, et al. Preparation of high porous silicon nitride foams with ultra-thin walls and excellent mechanical performance for heat exchanger application by using a protein foaming method. Ceram Int 2016, 42: 1713–1719.

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