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Synthesis of Silicon/Magnesium Silicon Nitride Diatom Frustule Replicas

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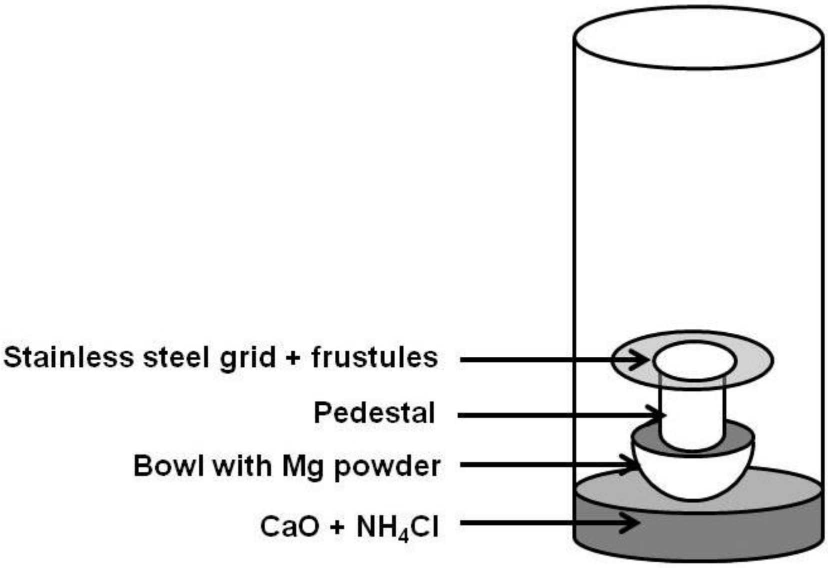

Fig. 1 Reactor Schematic

Fig. 1 illustrates the layout of the reactor utilized during synthesis of silicon/magnesium silicon nitride diatom frustules replicas. The tubular reactor is constructed of stainless steel featuring threaded end caps and allows for the reuse of the reactor. At the bottom of the reactor a mixture of calcium oxide (CaO) and ammonium chloride (NH_4Cl) is placed, upon heating this mixture generates ammonia (NH_3).

A stainless steel bowl is placed on top of the bottom layer, this bowl is filled with powdered magnesium (Mg) and generates Mg vapors upon heating above 650^{o}C. A hollow, stainless steel pedestal is placed on top of the Mg filled bowl and serves to create a distance between the frustules on top of the stainless steel grid and the other reactants, ensuring only vapors can contact the frustules during reaction. All reactants are transferred into the reactor within a glove box featuring argon (Ar) atmosphere.

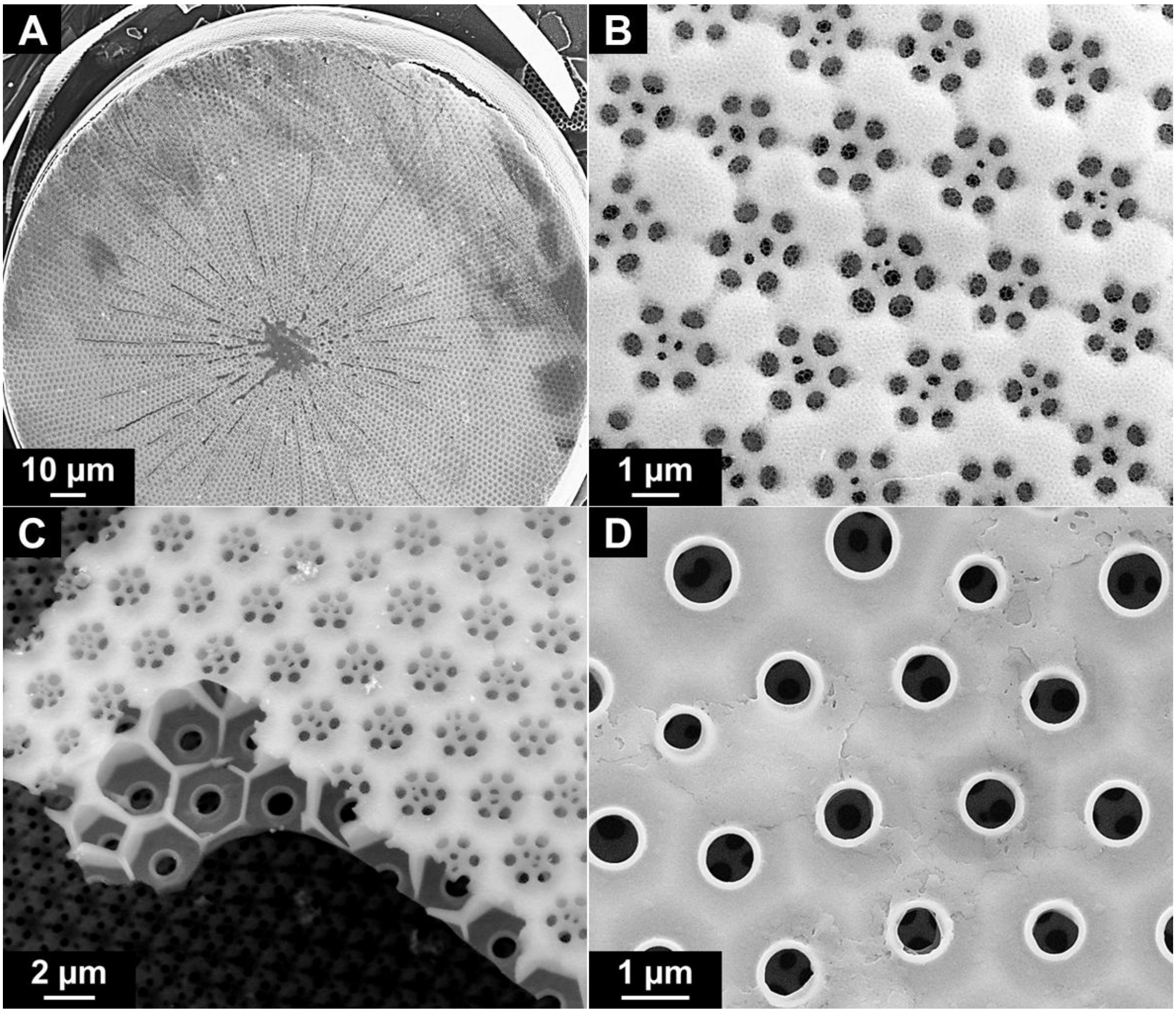

Fig. 2 *BSi* Frustules. Single valve (A); cribrum (B); cracked valve where the cribrum, areola and foramen can be observed(C), foramen (D)

Fig. 2 displays images of original, unreacted, biosilica (*BSi*) frustules, images were captured by scanning electron microscope (SEM). Fig. 2A, displays a single frustules valve. Fig. 2B displays the external layer of the frustule valve, called cribrum and features a structure of flower like patterns with hexagonal symmetry.

The pores of the cribrum are divided into smaller nano pores by thin silica branches. The areola (Fig. 2C), located just beneath the cribrum, features a honeycomb structure of bio-silica walls perpendicular to the cribrum. Each flower-like pattern of the cribrum is centered above a hexagonal cavity defined by the structure of the areola. Finally, the foramen (Fig. 2D) defines the inner side of the frustule valve and features a hexagonal array of circular pores.

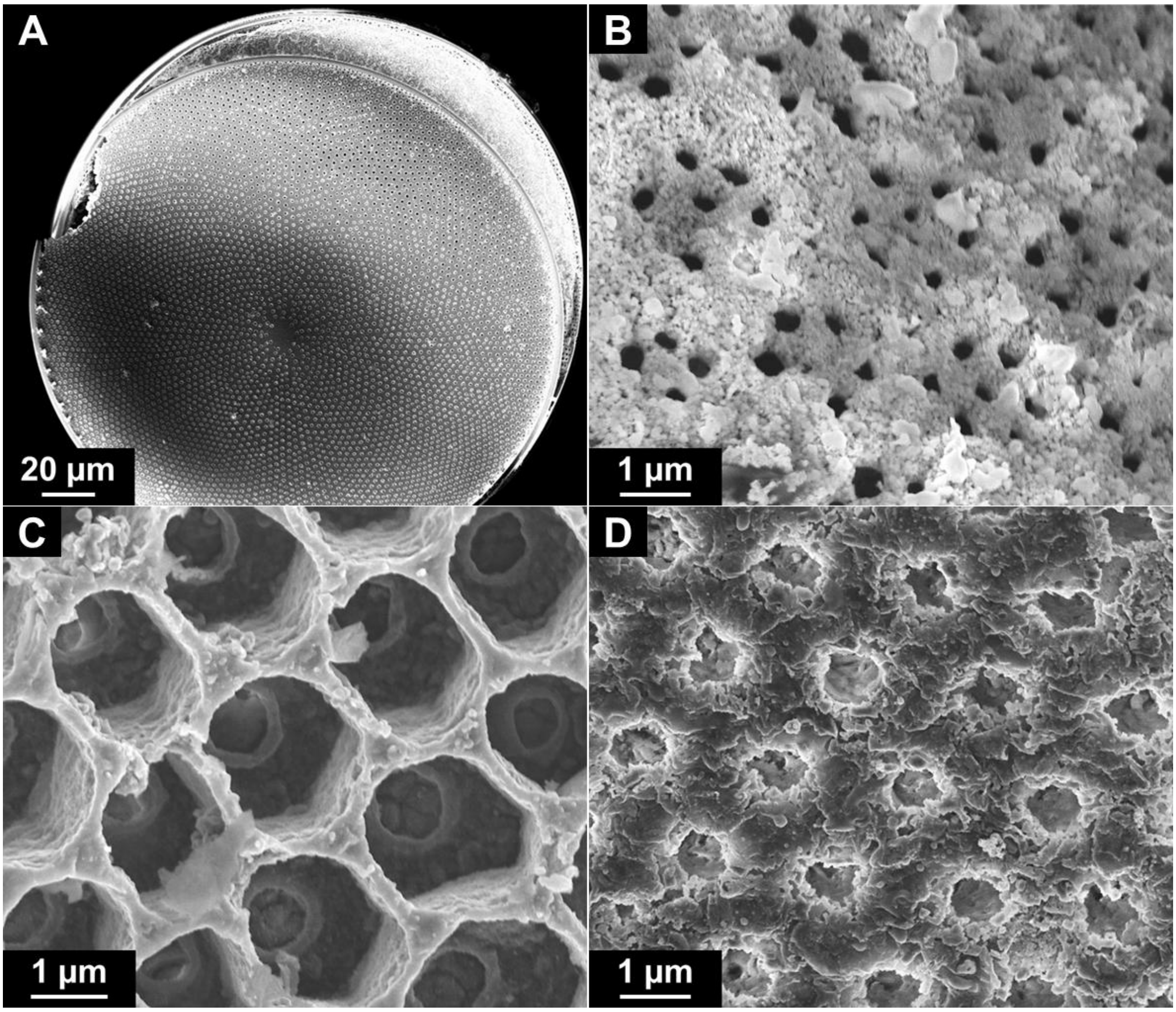

Fig. 3 *MSN* frustules. Structure of silicon/magnesium silicon nitride (*MSN*) frustule replicas. Images acquired by use of SEM. Two overlapping valves (A); cribrum (B); areola (C); foramen (D).

Fig. 3 displays the various structural aspects of silicon/magnesium silicon nitride (*MSN*) frustule replicas. Two overlapping *MSN*-frustule valves are observed in Fig. 3A. Their overall structural integrity appears to be well conserved compared to the *BSi*-frustule valve shown in Fig. 2A. The cribrum layer of a *MSN*-frustule is observed in Fig. 3B.

The surface of the valve has coarsened and the thin branches inside the pores have disappeared, but the typical flower-like porous pattern is retained. An *MSN*-frustule valve after stripping of the cribrum layer, leaves its areola clearly visible in Fig. 3C. The morphology of the areola layer is well conserved as compared to before any chemical transformation (cf. Fig. 2B). However, similarly to what is observed for the cribrum layer, a significant surface coarsening has taken place.

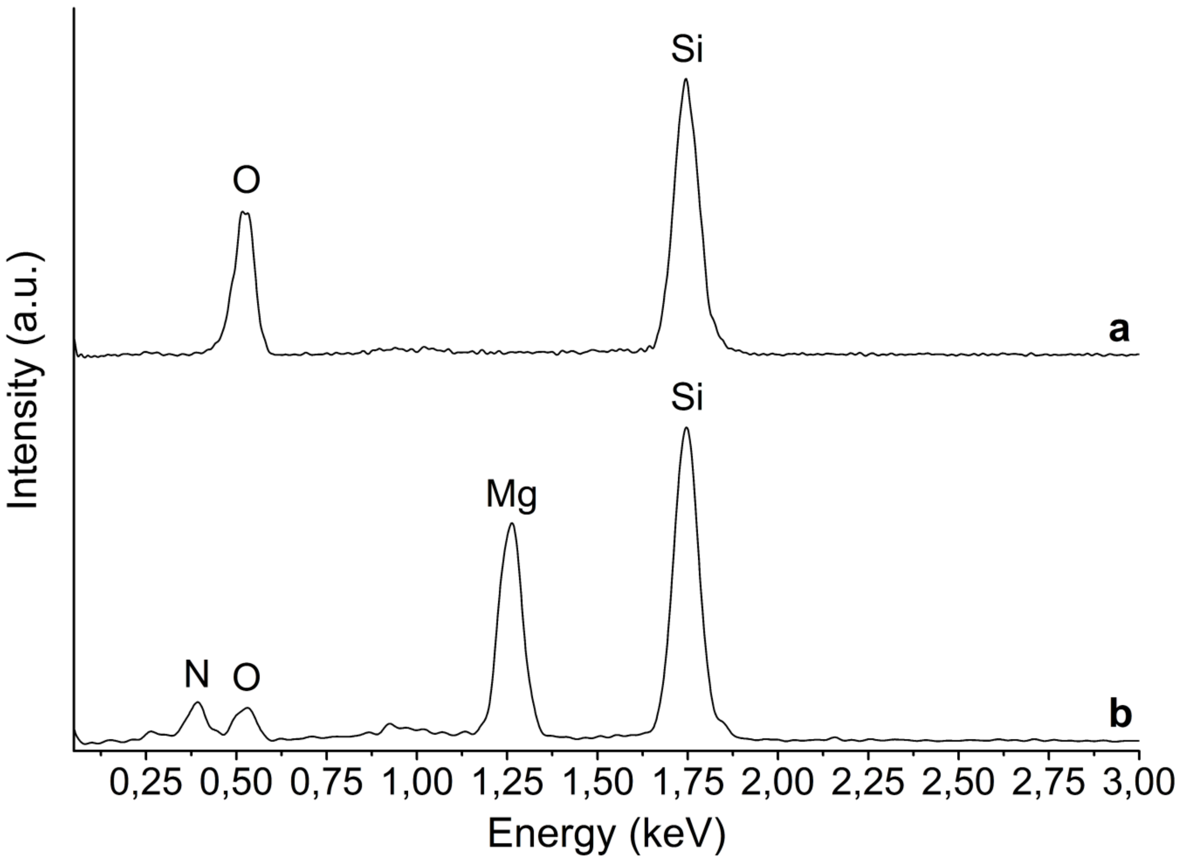

Fig. 4 EDS spectra. *BSi* frustules (a) and *MSN* frustules (b).

In Fig. 4A the EDS spectrum of a *BSi*-frustule is presented, and is consistent with biosilica (SiO_2) frustules. The main elemental constituents of the *MSN*-frustules appear to be silicon, magnesium, nitrogen and oxygen (cf. Fig. 4B).

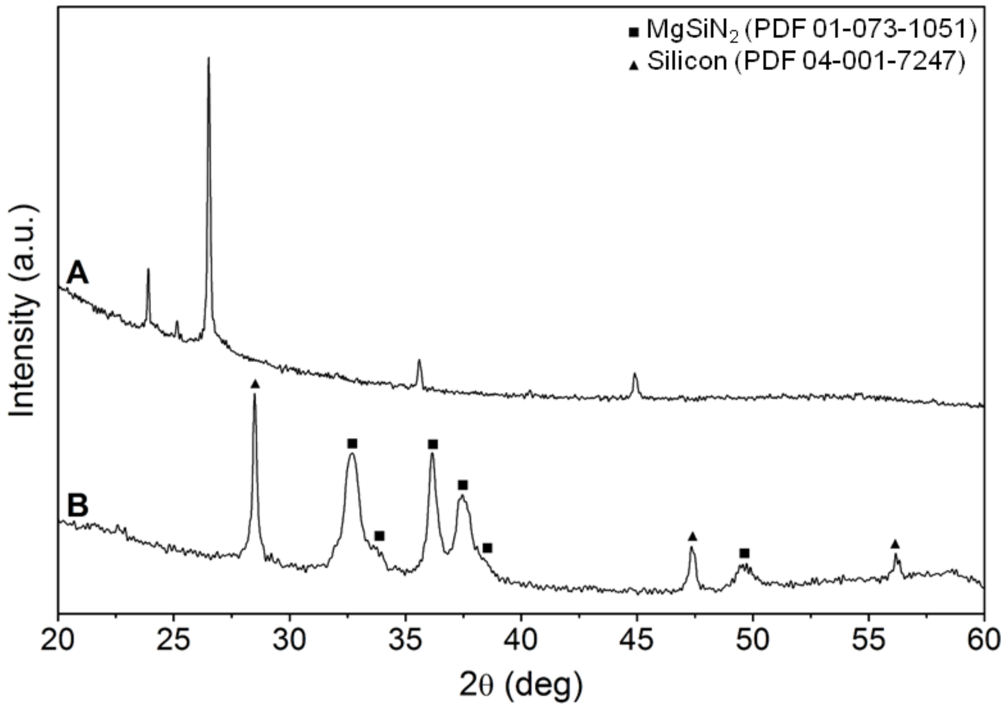

Fig. 5 XRD diffractograms. *BSi* frustules (A) and *MSN* frustules (B).

The XRD diffractogram of *BSi*-frustules is given in Fig. 5A. The diffraction peaks could not be unequivocally assigned to silica phases. The peak at 26.5° corresponds well with the main quartz peak (011), however all other quartz peaks are absent. Absence of selected reflections for powder X-ray diffraction analysis is often seen in cases of preferred orientation of highly oriented crystallites, but there is no evidence that would suggest such preferred orientation in this case.

The presence of amorphous material, presumably mainly silica, is however clearly evident, so it is considered most likely that the diffraction peaks are due to the presence of organic compounds or impurities. According to the results of the XRD analysis presented in Fig. 5B, the *MSN*-frustules consist of Si and $MgSiN_2$.

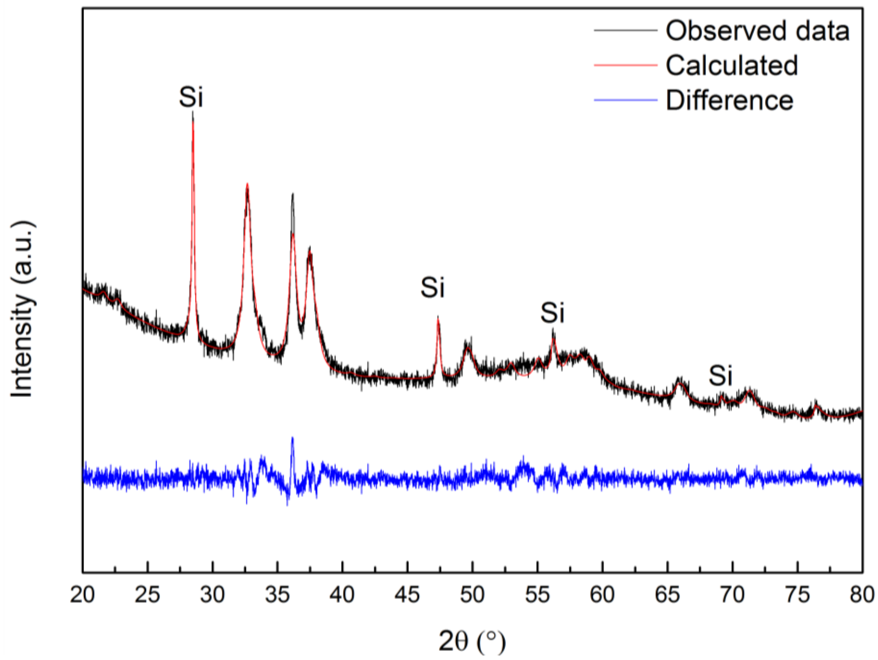

Fig. 6 Observed, calculated and difference plot for *MSN* frustules.

In Fig. 6, the observed, calculated and difference plot for MSN frustules is given. Rietveld analysis of the crystalline phases, suggests the content of MgSiN2 and Si to be approximately 94% and 6 wt%, respectively. The unit cell parameter of Si, M = 28.09, T = 293 K, refined in the cubic Fd-3m space group was 5.4316 Å. MgSiN2, M = 80.40, T = 293 K, was refined in the orthorhombic space group Pna21, with resulting unit cell parameters a = 5.3651 Å, b = 6.3844 Å and c = 4.9731. The final Rwp was 5.67. From visual inspection of the diffractogram, the amorphous phase appears to have disappeared after nitriding.