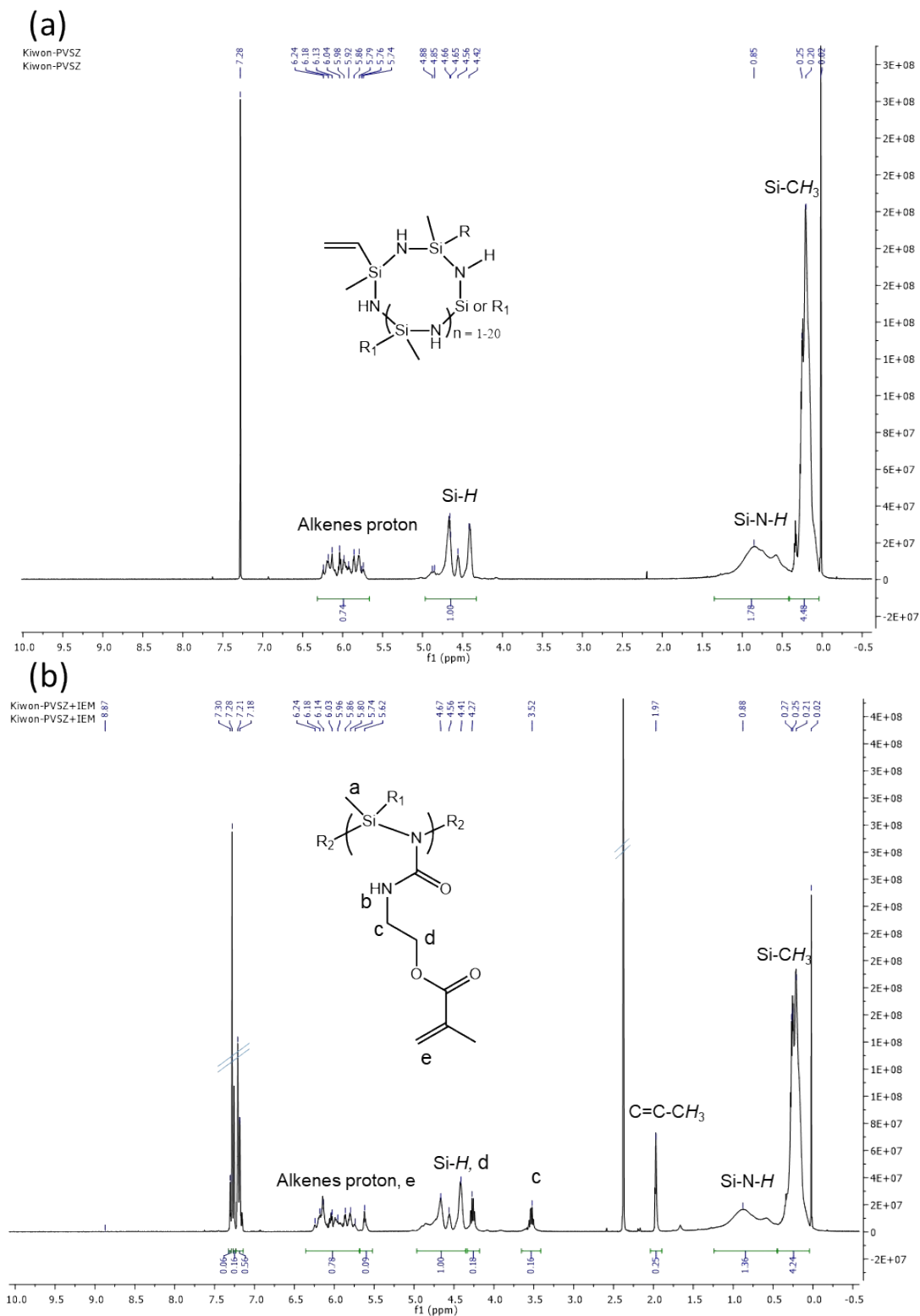


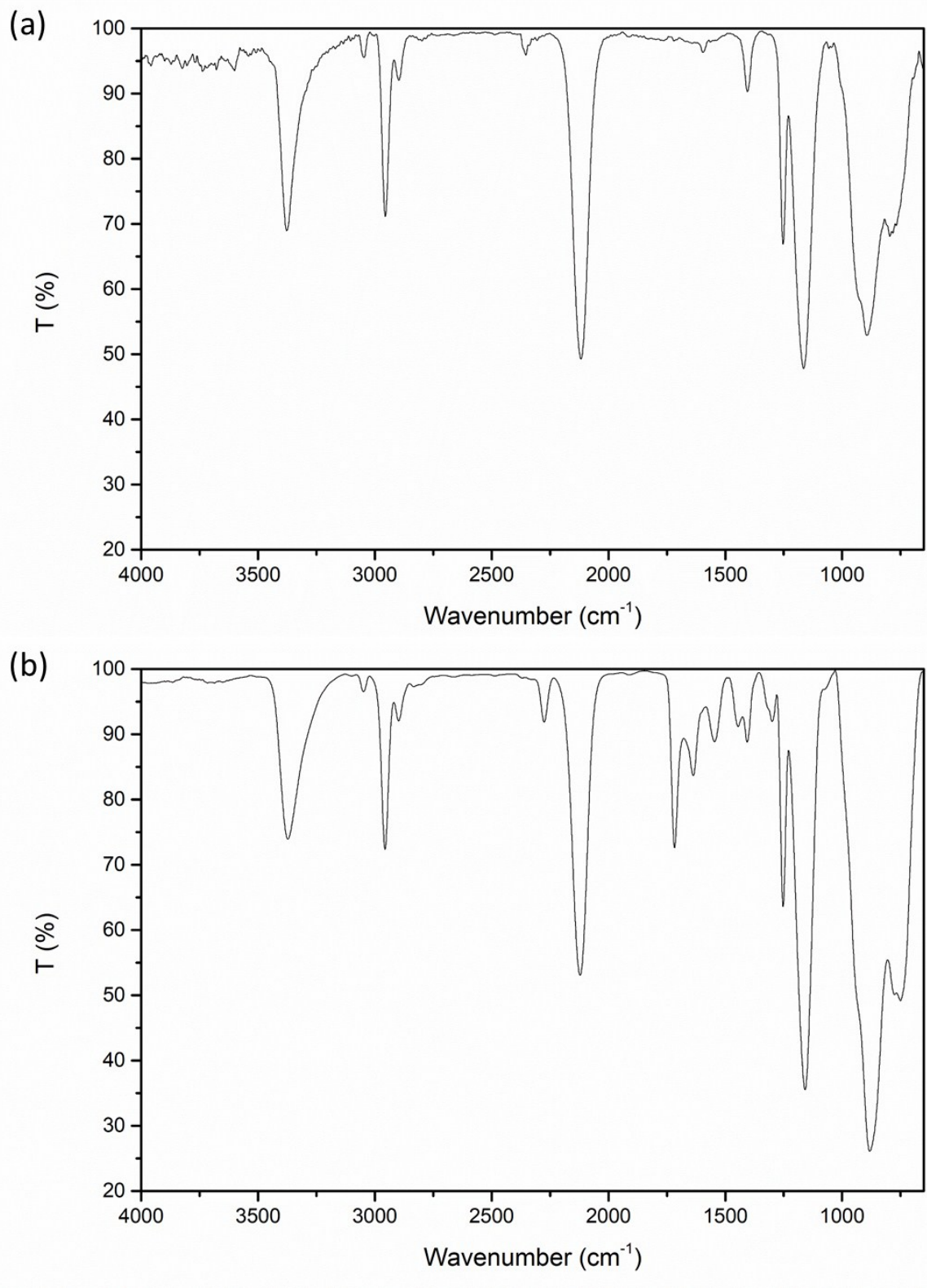
## Supporting Information

# 3D-printed Monolithic SiCN Ceramic Microreactors from a Photocurable Preceramic Resin

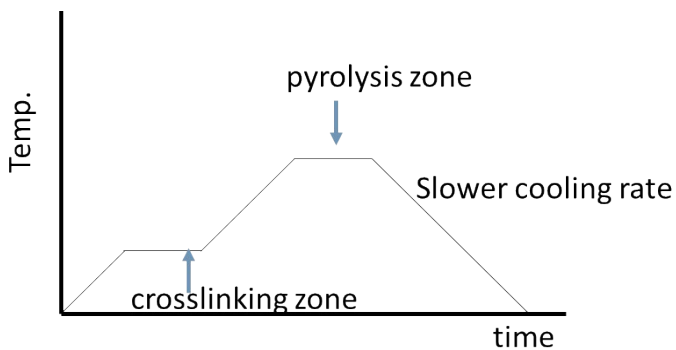
Ki-Won Gyak, Niraj K. Vishwakarma, Yoon-Ho Hwang, Jee Hwan Kim, Hui-suk Yun and Dong-Pyo Kim\*



**Fig. S1**  $^1\text{H-NMR}$  spectra of (a) pristine PVSZ and (b) mPVSZ. The peaks from  $\delta=7.18-7.30$  and  $\delta=2.3$  comes from toluene used as a solvent for resin modification process.

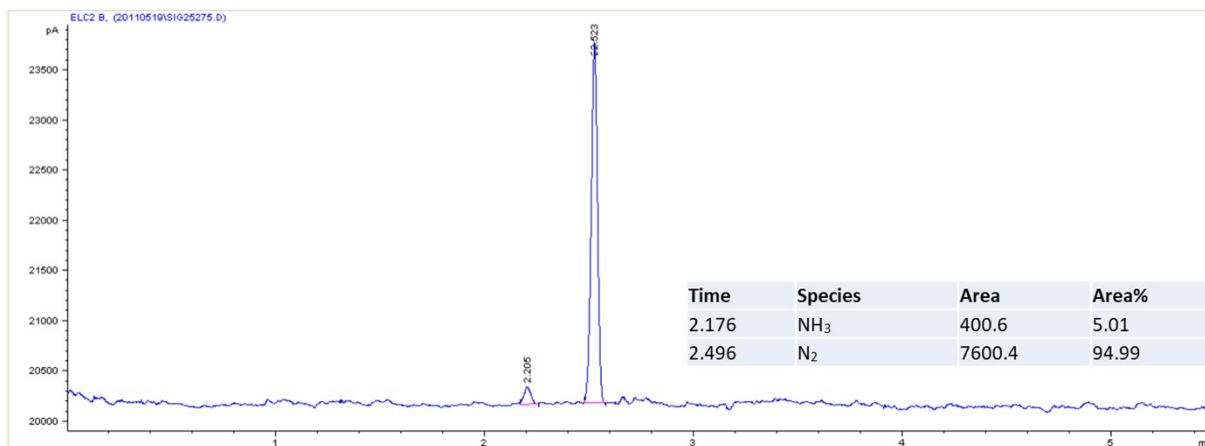


**Fig. S2** FT-IR spectra of (a) pristine PVSZ and (b) mPVSZ

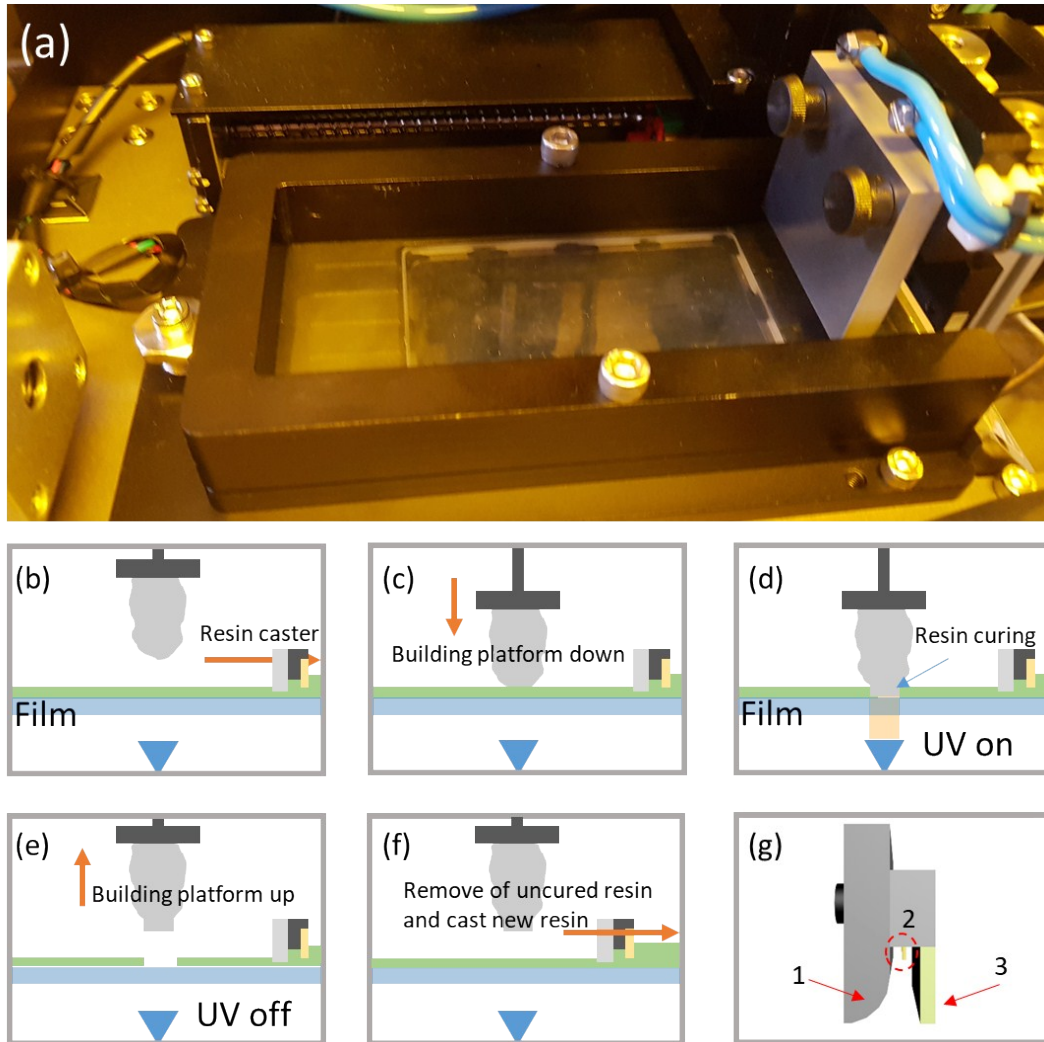


Temp.: 300 -> 1000 °C  
 Elevation ratio: 1 °C / min  
 Heating time: 3 hr each  
 Cooling ratio: 1 °C / min  
 Under Ar atmosphere

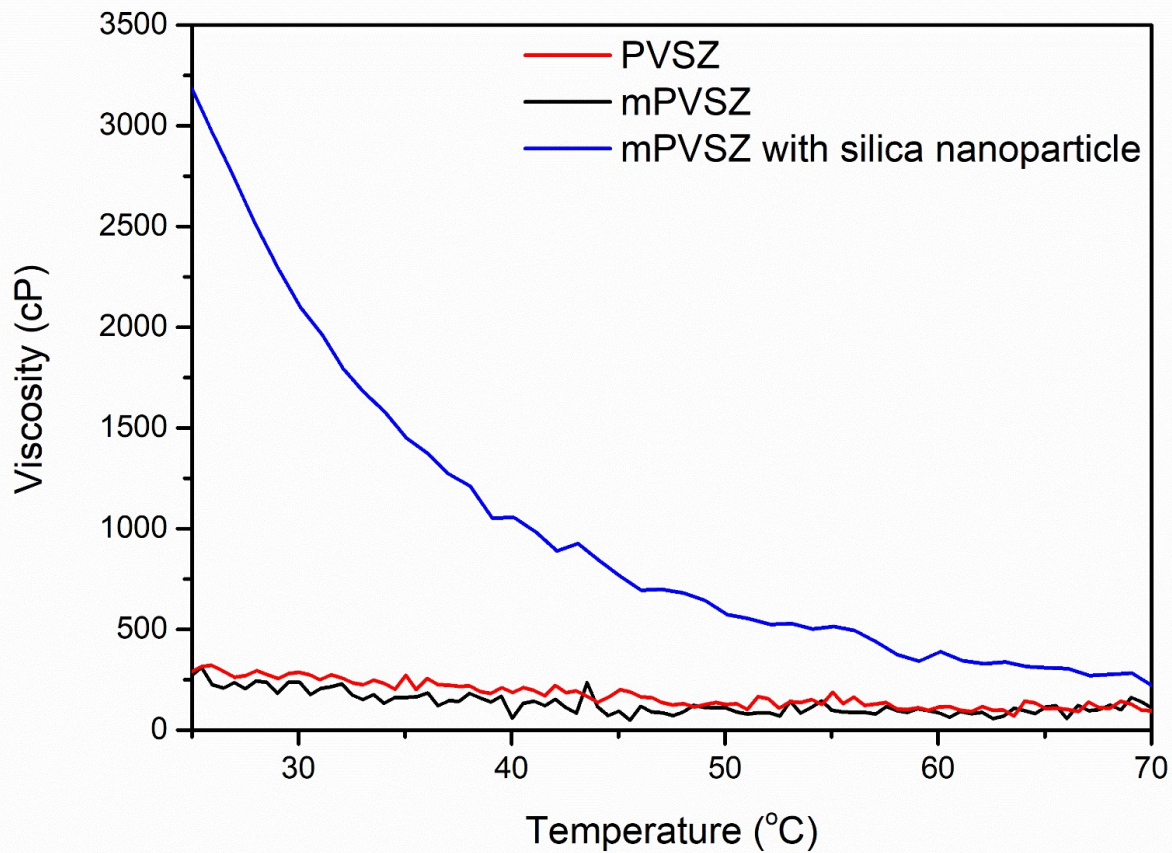
**Fig. S3** Heating profile for pyrolysis of the mPVSZ green body into SiCN ceramic monoliths, and applied the same to powder samples.



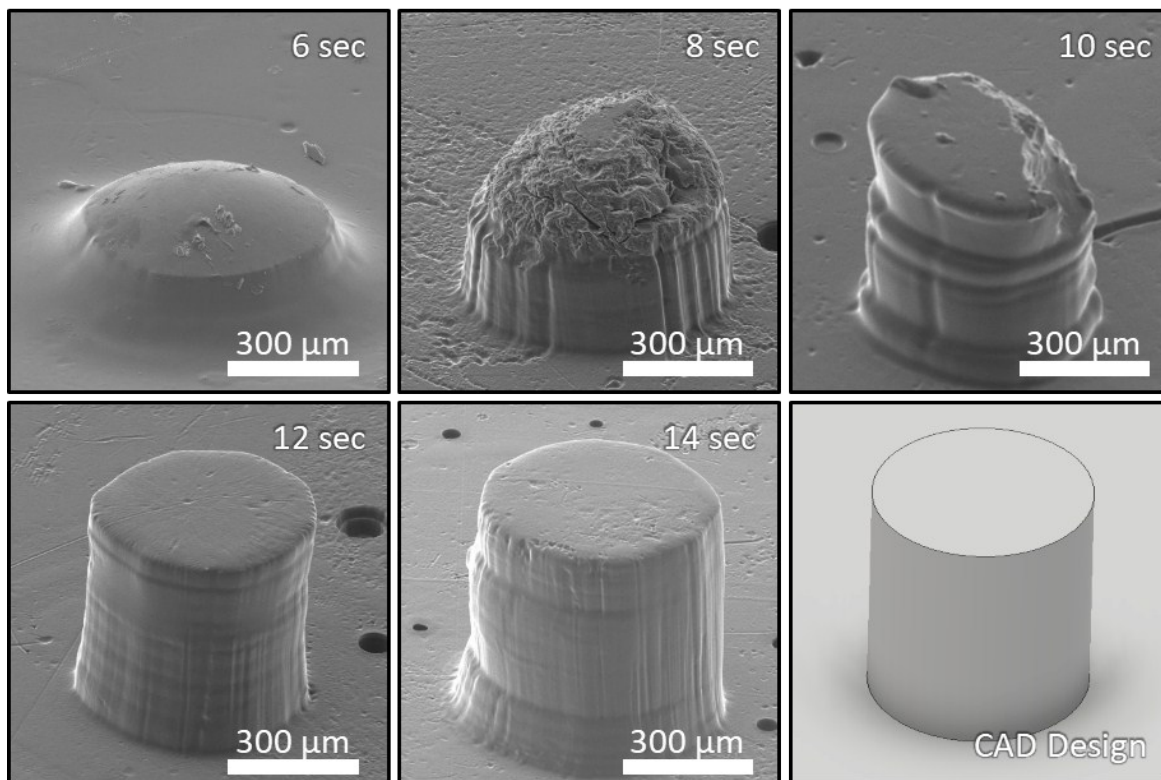
**Fig. S4** Exemplary GC result of the product obtained from ammonia cracking at 1000 °C with 8 mL min<sup>-1</sup> inlet flow rate in the SiCN ceramic microreactor.



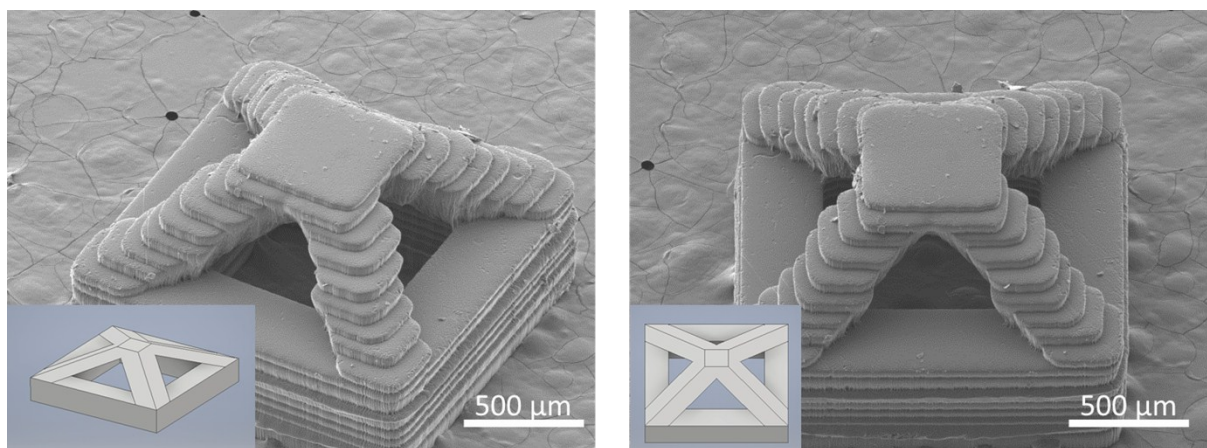
**Fig. S5** (a) photograph of in-house 3D-printer and (b-g) Schematic illustration for printing principle of the in-house 3D-printer. (b) cast a resin layer on the UV transparent film. (c) approach a building platform to the casted resin. (d) radiate the patterned UV to cure the resin. (e) turn off the UV and lift up the patterned layer on the platform. (f) remove the uncured resin and cast a fresh resin layer on the film. (g) detailed scheme of resin blade and supplier. 1. a blade to cast resin with specific thickness on the film. 2. a nozzle to supply resin. 3. a blade to remove the uncured resin on the film.



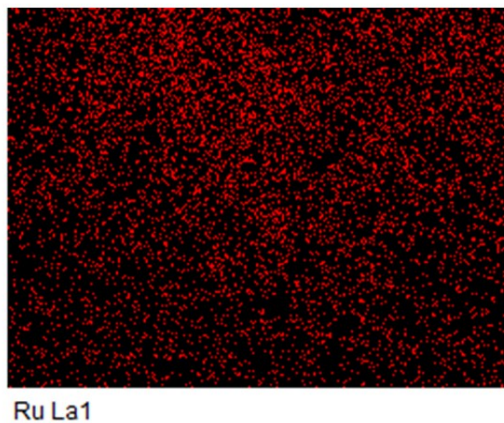
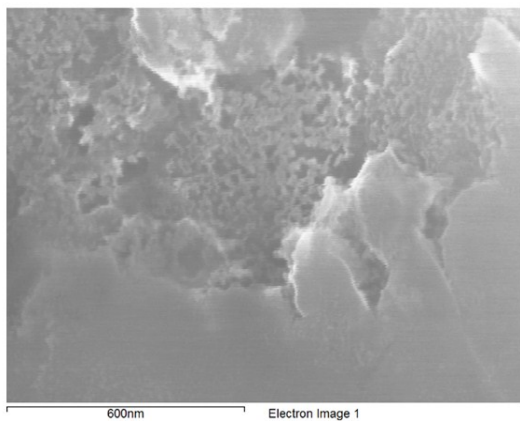
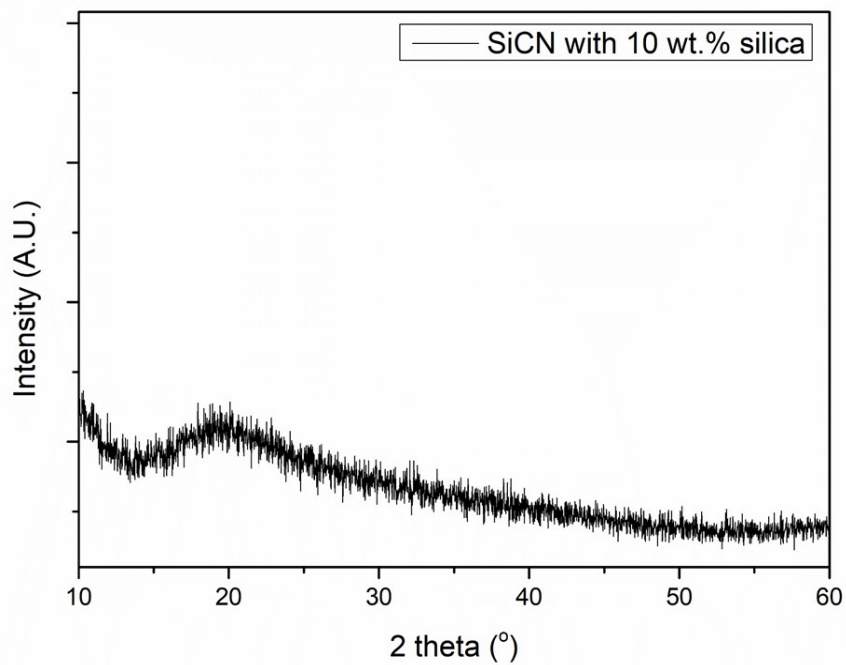
**Fig. S6** Viscosity of pristine PVSZ, modified PVSZ (mPVSZ), mixed mPVSZ with 10 wt.% of silica nanoparticle filler, along temperature.



**Fig. S7** Optimization of UV exposure time in range 6 ~ 14 sec for curing each digital mask (40  $\mu\text{m}$  thickness) of a simple pillar structure (500  $\mu\text{m}$  diameter and 750  $\mu\text{m}$  height).

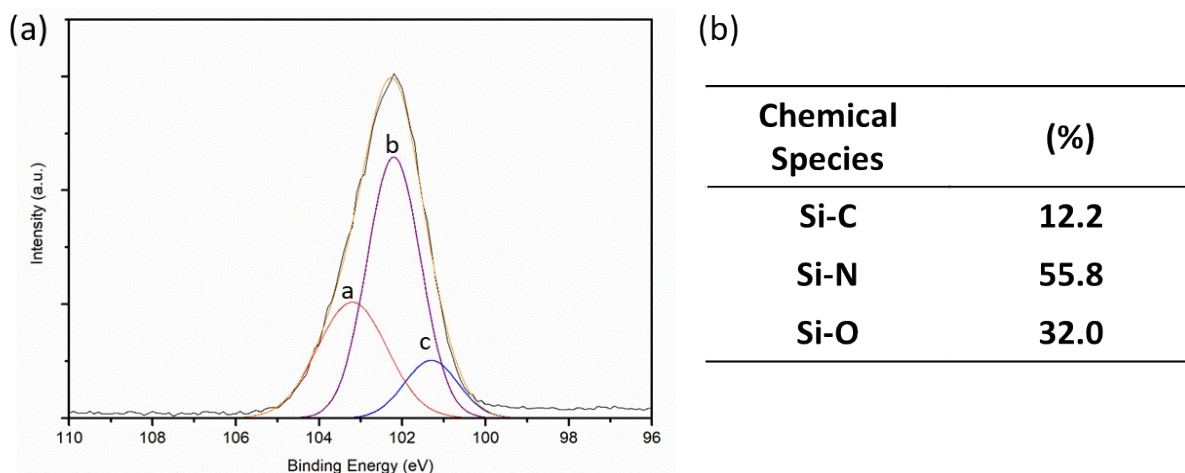


**Fig. S8** 3D-printed mPVSZ green body structures to show the printing resolutions.

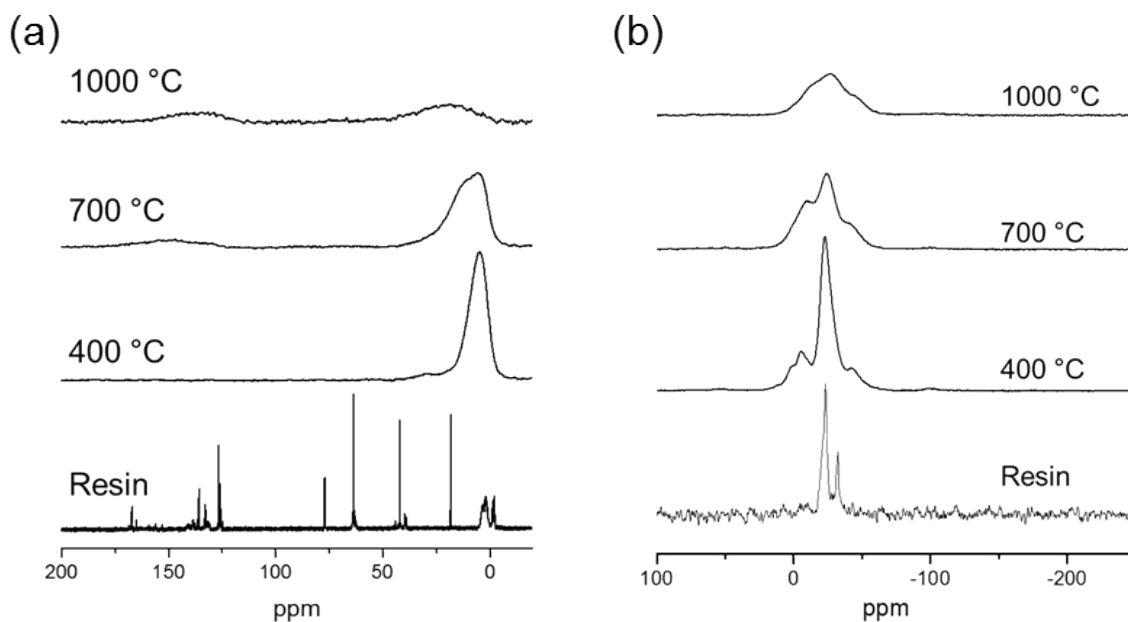


**Fig. S9** (a) amorphous XRD pattern of the pyrolyzed mPVSZ containing 10 wt.% of silica nanoparticles at 1000 °C for 3 h under Ar. (b-c) EDX mapping of the immobilized Ru catalyst on surface of the pyrolyzed SiCN ceramic.

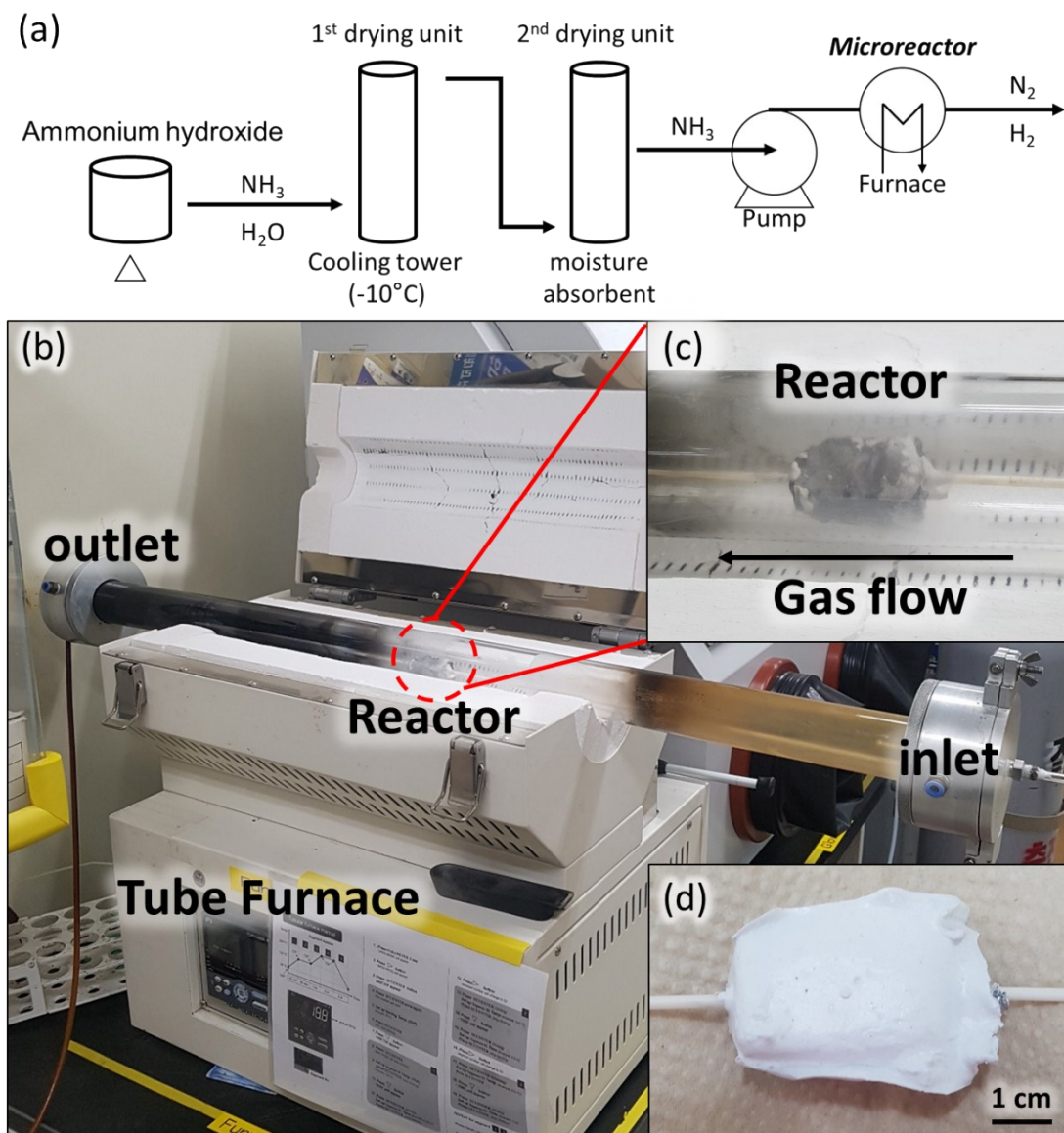




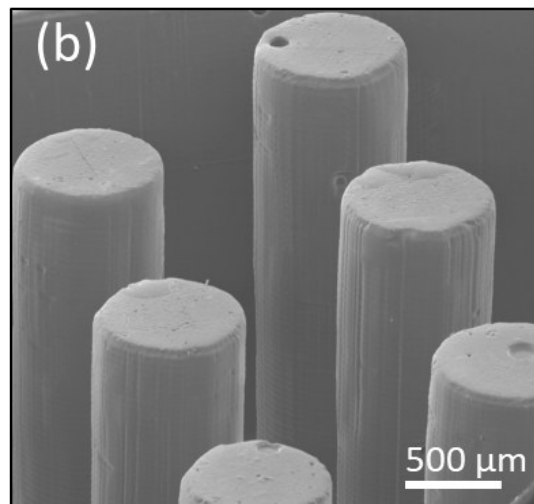
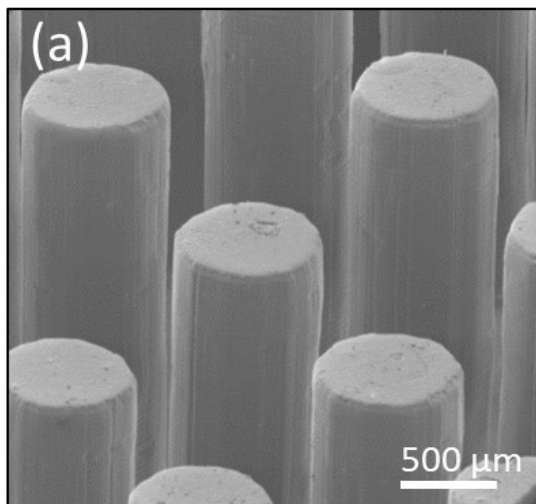
**Fig. S10** (a) XPS Si2p spectra of the pyrolyzed mPVSZ containing 10 wt.% of silica nanoparticles at 1000 °C for 3 h under Ar. The deconvoluted peaks are a) Si-N, b) Si-O, and c) Si-C. (b) Atomic percentage of each chemical species from the deconvoluted Si2p spectra.



**Fig. S11** Solid-state NMR spectra of pristine mPVSZ and the pyrolyzed mPVSZ at different temperatures under argon atmosphere: (a)  $^{13}\text{C}$  NMR; (b)  $^{29}\text{Si}$  NMR



**Fig. S12** (a) Schematic diagram and (b) set-up for ammonia cracking test, and (c) a SiCN ceramic microreactor placed into quartz tube of furnace, (d) a SiCN ceramic microreactor connected with aluminar inlet/outlet tubes, entirely sealed with ceramic paste.



**Fig. S13** SEM images of micropillars in the SiCN ceramic microreactors. (a) As-pyrolyzed at 1000 °C under Ar, before the reaction, (b) after  $\text{NH}_3$  gas exposure at 1000 °C for 48 h.