

# **Sturdy, Monolithic SiC and Si<sub>3</sub>N<sub>4</sub> Aerogels from Compressed Polymer-Crosslinked Silica Xerogel Powders**

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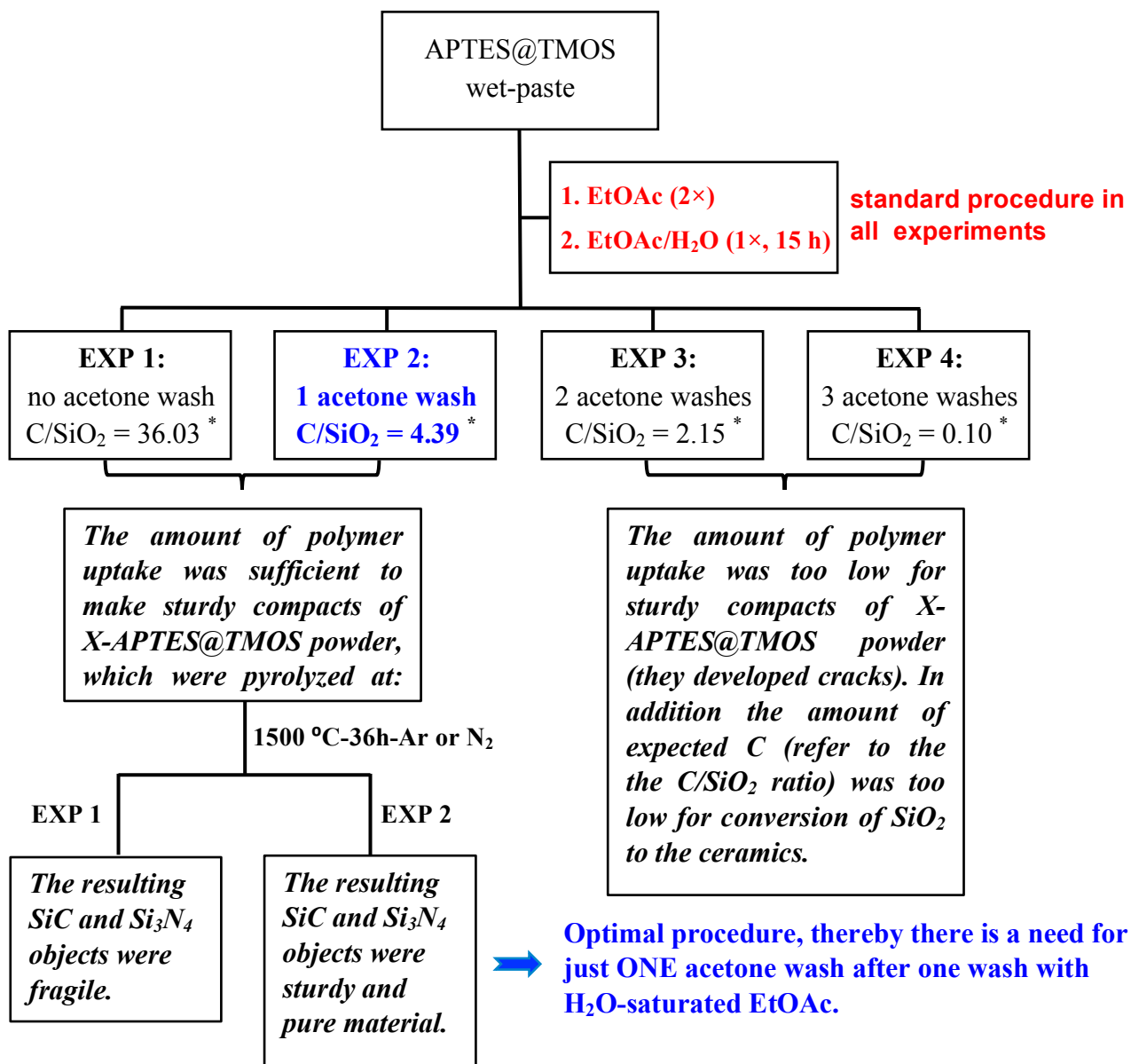
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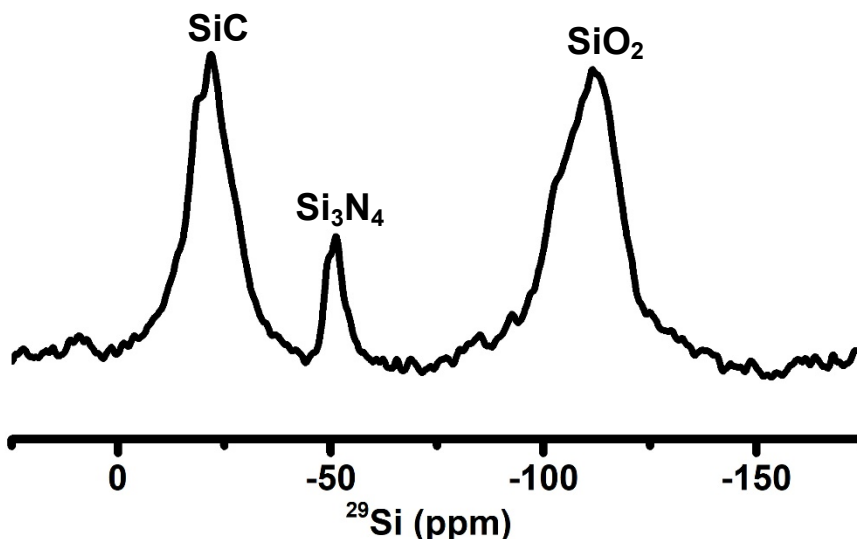
## Appendix I. Optimization of washing procedures for an optimal amount of carbon available for carbothermal reduction

Scheme S.1. Optimization of washing procedure for optimal polymer uptake during crosslinking, and thereby optimal amount of carbon produced and available for carbothermal reduction

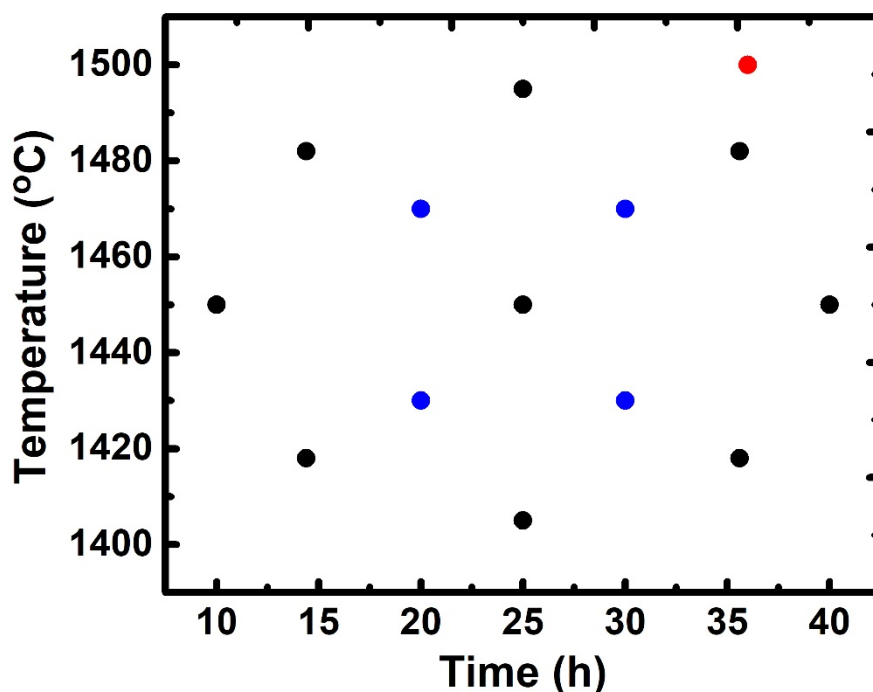


\* This is the amount of carbon relative to silica that is expected based on the carbonization yield of TIPM-derived polyurea (56% w/w, by pyrolysis at 800 °C/Ar) and the amount of polyurea in the resulting X-APTES@TMOS powder determined with TGA (as in Figure 3 of the main article.)

## Appendix II. Optimization of pyrolytic conditions for converting compressed silica compacts to $\text{Si}_3\text{N}_4$ aerogels



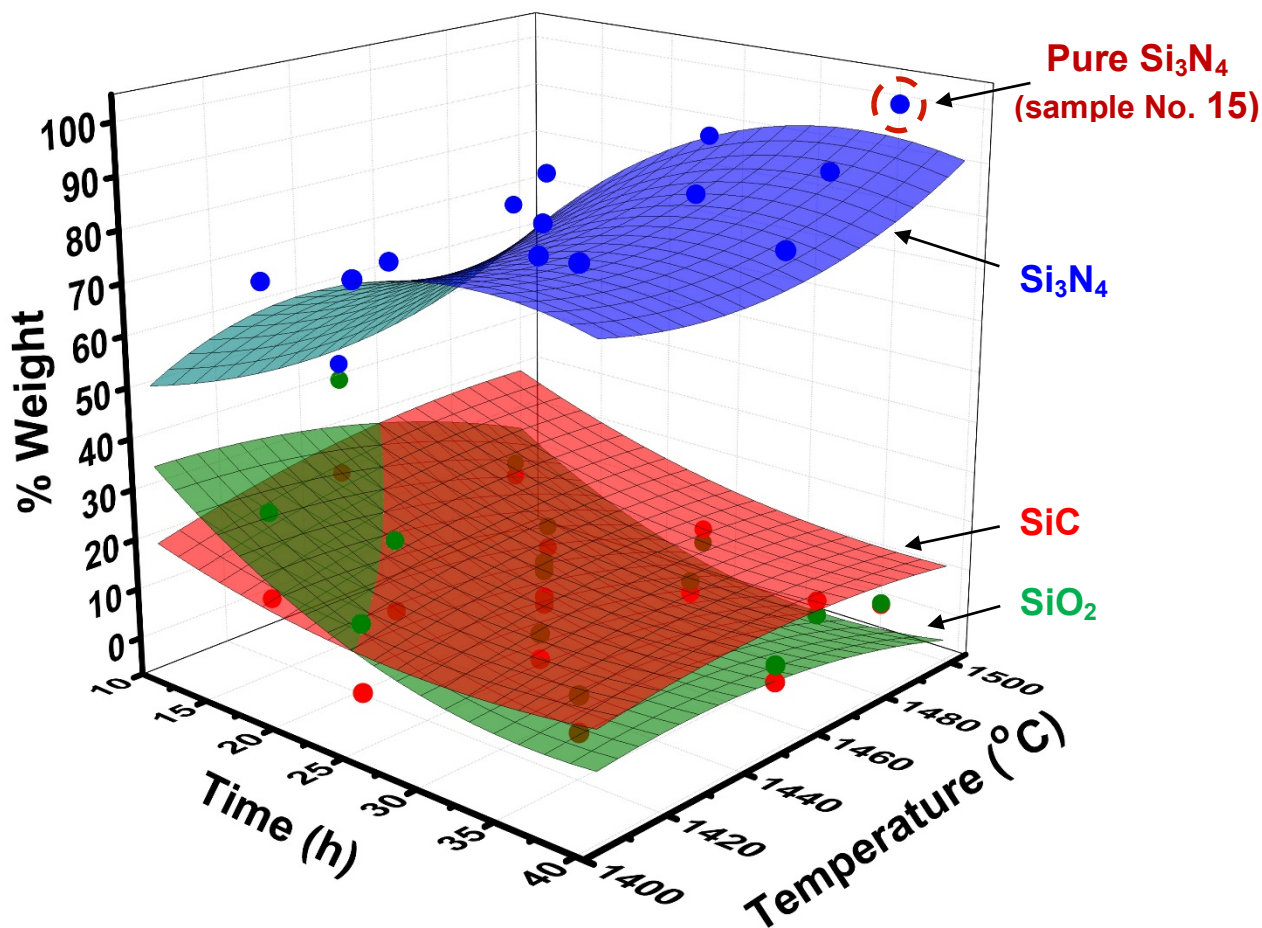
**Figure S.1.** Solid-state MAS  $^{29}\text{Si}$  NMR of a mixture consisting of  $\text{SiC}:\text{Si}_3\text{N}_4:\text{SiO}_2$  in a ratio of 1:1:1 mol:mol:mol, using a ZrO rotor spun at 7kHz and direct polarization (zg pulse sequence). Acquisition parameters: number of scans: 16384; relaxation delay: 5 sec; acquisition time: 0.0129 sec; power level for pulse: 250 W. Integrated areas:  $\text{SiC}$ : 39.02;  $\text{Si}_3\text{N}_4$ : 7.77;  $\text{SiO}_2$ : 53.02.



**Figure S.2.** Samples prepared in order to identify the optimal conditions (pyrolysis temperature and time) for  $\text{Si}_3\text{N}_4$ . Black points: samples suggested by a Central Composite Rotatable Design (CCRD) statistical method. Blue points: extra points added to the CCRD design in order to increase confidence. Red point: conditions predicted to produce pure  $\text{Si}_3\text{N}_4$ .

**Table S.1.** Quantitative analysis using solid-state  $^{29}\text{Si}$  NMR under the conditions indicated in the legend of Figure S.1 of samples prepared by pyrolysis of X-APTES@TMOS compacts according to the conditions of Figure S.2.

Sample	Pyrolysis Time - Temperature	Quantitative Analysis from NMR (Lorentzian fitting)			
		wt% $\text{Si}_3\text{N}_4$	wt% SiC	wt% $\text{SiO}_2$	Mole Ratio [ $\text{Si}_3\text{N}_4$ ] : [SiC] : [ $\text{SiO}_2$ ]
1	10 h – 1450 °C	42.15	19.04	38.81	1 : 1.58 : 2.15
2	14.39 h – 1418 °C	69.38	6.55	24.07	1 : 0.33 : 0.81
3	14.39 h – 1482 °C	71.14	13.02	15.84	1 : 0.64 : 0.52
4	20 h – 1430 °C	74.24	5.73	20.03	1 : 0.27 : 0.63
5	20 h – 1470 °C	83.14	6.18	10.68	1 : 0.26 : 0.30
6	25 h – 1405 °C	79.83	3.42	16.75	1 : 0.15 : 0.49
7	25 h – 1450 °C	80.37	5.52	14.11	1 : 0.24 : 0.41
8	25 h – 1450 °C	80.47	7.13	12.40	1 : 0.31 : 0.36
9	25 h – 1495 °C	88.72	7.10	4.18	1 : 0.28 : 0.11
10	30 h – 1430 °C	81.88	6.55	11.57	1 : 0.28 : 0.33
11	30 h – 1470 °C	84.96	6.31	8.73	1 : 0.26 : 0.24
12	35.61 h – 1418 °C	86.97	2.98	10.05	1 : 0.12 : 0.27
13	35.61 h – 1482 °C	90.10	6.43	3.47	1 : 0.25 : 0.09
14	40 h – 1450 °C	85.06	5.83	9.11	1 : 0.24 : 0.25
15	36 h – 1500 °C	99.68	0	0.32	1 : 0.00 : 0.007



**Figure S.3.** Fitting the weight percent data for SiC, Si<sub>3</sub>N<sub>4</sub> and unreacted SiO<sub>2</sub> (from Table S.1) in samples produced by pyrolysis of X-APTES@TMOS compacts for the time periods ( $t$ ) and at the specific temperatures ( $\theta$ ) as indicated. The fitting equations are:

$$\%SiC = (0.022_1)t^2 + (-0.001_4)\theta^2 + (-0.004_2)t\theta + (4.66_9)t + (4.30_7)\theta + (-319_9)$$

$$R^2 = 0.82904$$

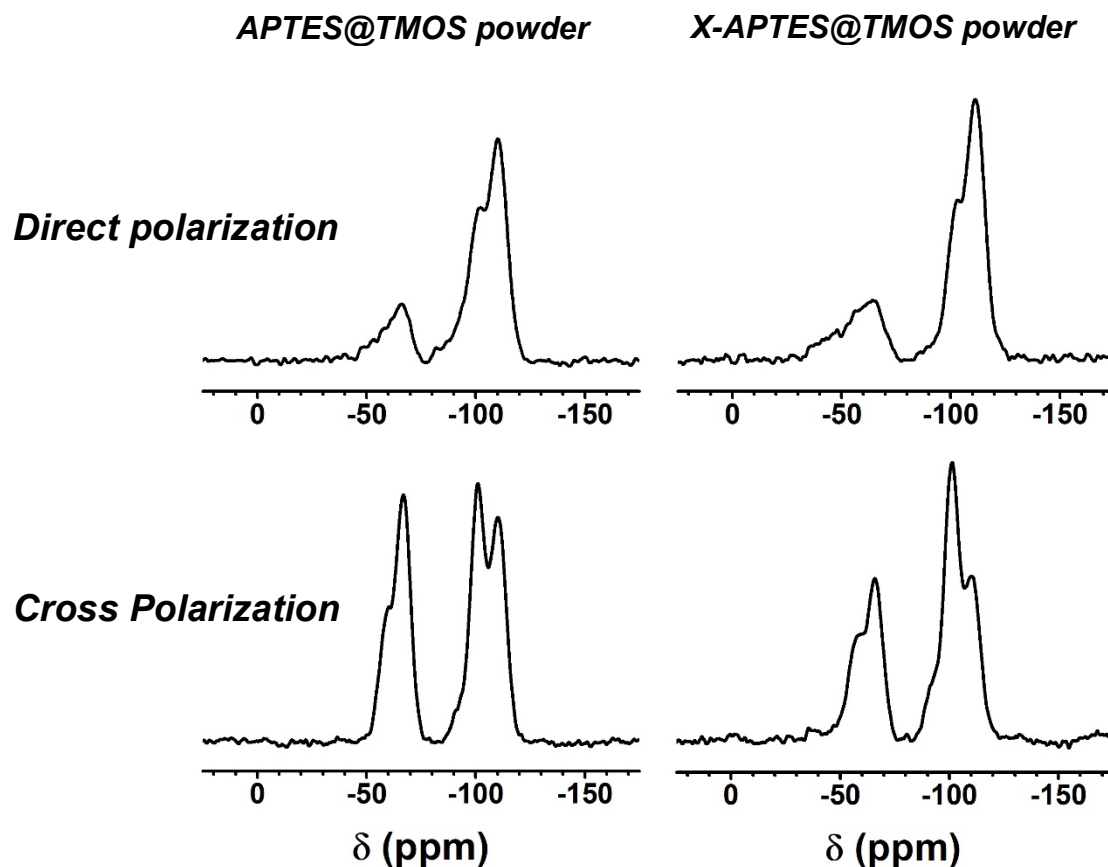
$$\%Si_3N_4 = (-0.063_6)t^2 + 0.003_4\theta^2 + (0.001_1)t\theta + (2.73_5)t + (-9.80_7)\theta + (707_8)$$

$$R^2 = 0.91297$$

$$\%SiO_2 = (0.042_5)t^2 + (-0.002_9)\theta^2 + (0.003_1)t\theta + (-7.39_4)t + (5.50_0)\theta + (-378_0)$$

$$R^2 = 0.93479$$

**Appendix III. Solid-state  $^{29}\text{Si}$  NMR of APTES@TMOS and of X-APTES@TMOS under two different acquisition conditions**



**Figure S.4.** Solid-state  $^{29}\text{Si}$  NMR data for the two materials as indicated taken using two different modes: Direct and cross-polarization (CP). Note the enhancement of Q3 and T2 under CP, and the even higher enhancement of Q3 relative to Q4 after crosslinking, signifying that the TIPM-derived crosslinking polymer (polyurea) latches not only on APTES-provided  $-\text{NH}_2$  groups, but also on  $-\text{OH}$  groups of Q3 positions.