

Supporting information

A straightforward approach to high purity sodium silicide Na_4Si_4

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Table S1 Comparison of reported syntheses towards Na₄Si₄

Reactants	Setup	Ball-milling time	Reaction time	Reaction temperature	Purity	Purification procedure	Ref.
NaH+Si nanoparticles Na in 10 mol.% excess	Covered h-BN crucible in a quartz tube	2min	24h	395°C	98%	/	This work
NaH+Si Na in 90 mol.% excess	Covered alumina crucible in a silica glass tube	30min	48h	420°C	Na detected by XRD	/	30
NaH+Si Na in 60 mol.% excess	Covered alumina crucible	1h	48h	395°C	/	Excess Na removed by vacuum at 250°C for 3h	19
Na+Si Na in slight excess	Ta crucible sealed in stainless steel tube	/	72h	650°C	/	Excess Na removed by evacuation at 300°C for 6h	7
Na+Si Na in 10 mol.% excess	Nb tube welded with Ar arc welder, sealed in fused silica jacket	/	83h	650°C	/	Excess Na removed by vacuum sublimation at 300°C	25
Na+Si Na in excess	Closed Ta container sealed in evacuated quartz glass ampoule	/	100h	750°C	/	Excess Na removed by vacuum distillation at 230 °C and 5.10 ⁻⁶ mbar	23
Na+Si Na in 6 mol.% excess	Ni crucible sealed in steel autoclave	/	30-40h	650°C	/	Excess Na removed at 240°C for 15-20h	26
Na+Si Na in 10 mol.% excess	W crucible sealed in stainless steel canister	/	36h	650°C	Na in excess	/	27
Na+Si Stoichiometric mixture	Sealed Ta tube	/	1h10min	800-1200°C	44% (Si in excess)	/	6
Na+silica gel	Sealed Erlenmeyer flask	/	/	400°C	15%	/	28

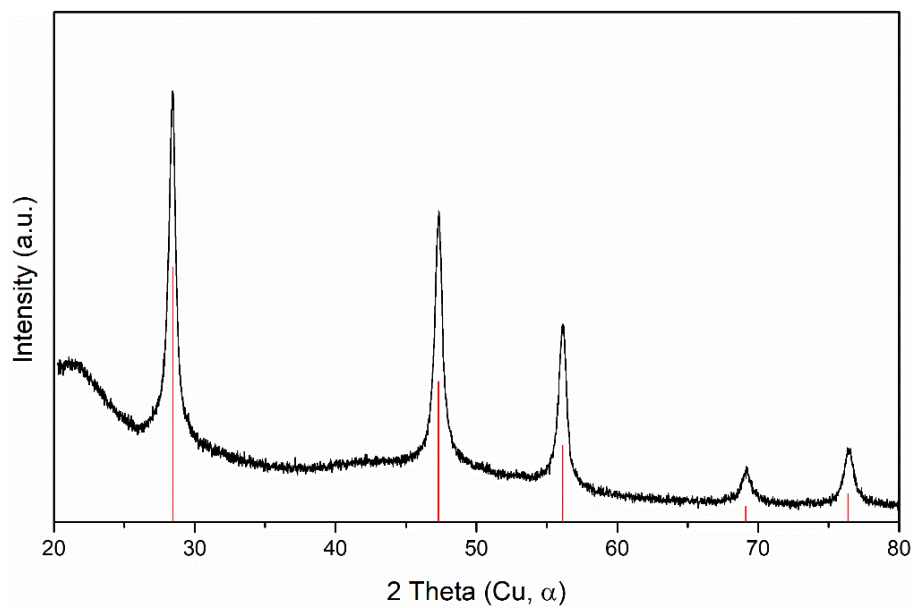


Figure S1. Powder XRD pattern (bottom) of Si nanoparticles used as reagents. The XRD pattern is indexed along the silicon diamond structure (red bars).

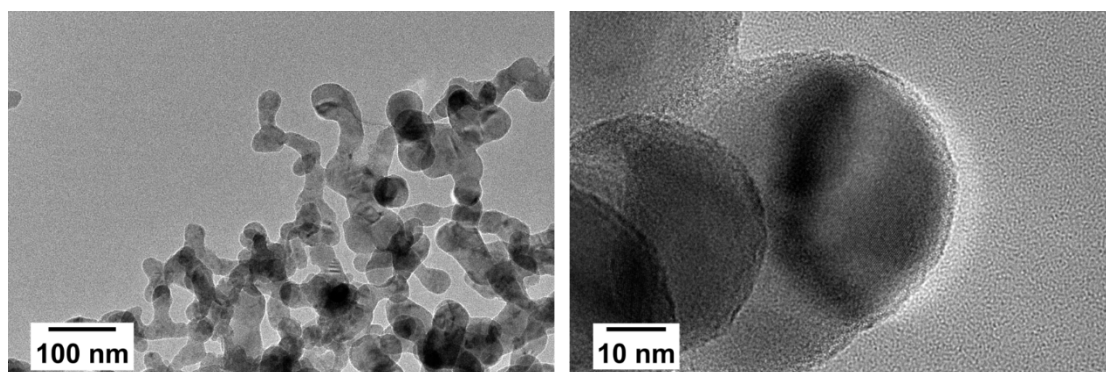


Figure S2. TEM images of as-received Si nanoparticles used as reagents.

Table S2. Na₄Si₄ lattice parameters obtained by Le Bail analysis of the XRD pattern of the powder obtained at 395 °C for 24 h under 55 mL min⁻¹ Ar flow for a NaH:Si = 1.1:1 mol. reagent ratio.

	Na ₄ Si ₄	NaOH
S.G.	<i>C2/c</i>	<i>Cmcm</i>
a (Å)	12.1727(2)	3.3990(1)
b (Å)	6.5684(1)	11.4366(6)
c (Å)	11.1442(1)	3.4054(1)
β (°)	119.1546(9)	
χ ²	4.22	

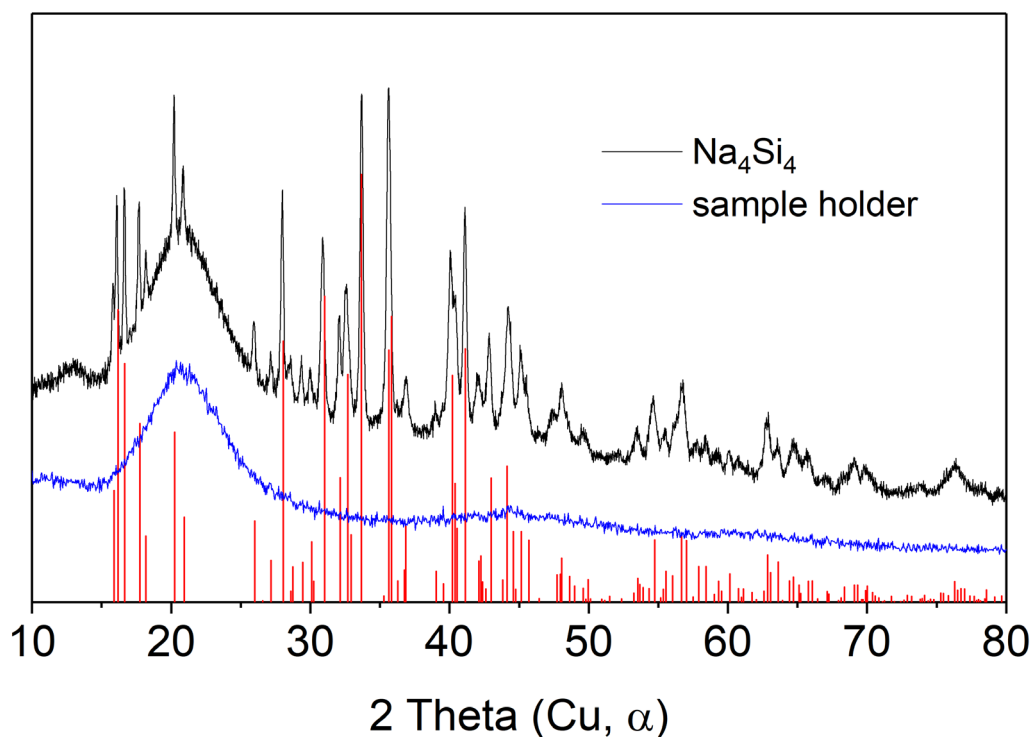


Figure S3. Quickly acquired (5 min) powder XRD pattern of the Na₄Si₄ sample obtained at 395 °C for 24 h under 55 mL min⁻¹ Ar flow for a NaH:Si = 1.1:1 mol. reagent ratio. Red drop lines indicate Na₄Si₄ reference. The blue line shows the experimental diagram recorded for the empty sample holder equipped with the scattering plastic dome. The absence of a peak at 38.2° (2theta Cu Kα) indicates the absence of crystalline NaOH.

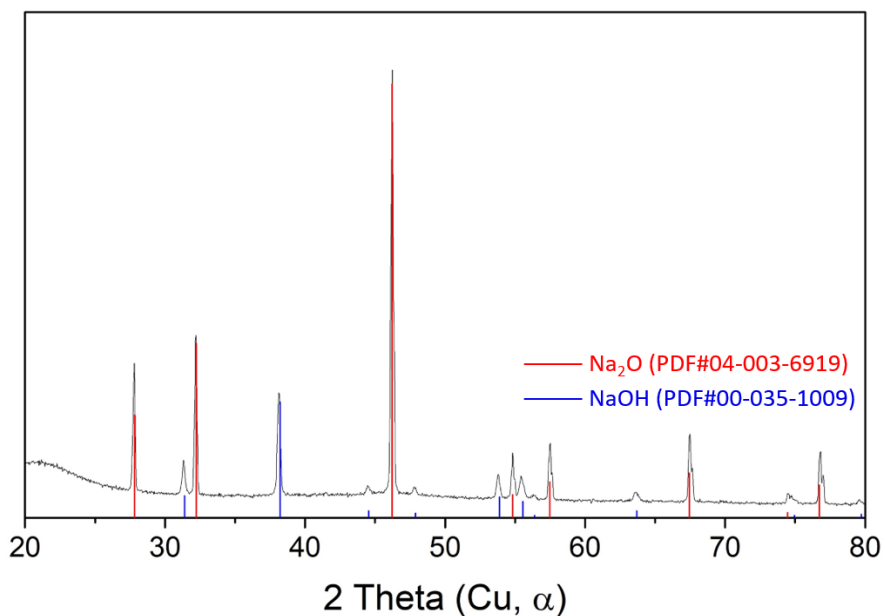


Figure S4. Powder XRD pattern of the white pellet on the top of the as-prepared product of Na_4Si_4 synthesis.

Table S3. Lattice parameters obtained by Le Bail analysis of the XRD pattern of the clathrate powders obtained by Na_4Si_4 thermal decomposition at 470 and 440 °C.

	S.G	$a_{470^\circ\text{C}}$ (Å)	$a_{440^\circ\text{C}}$ (Å)
$\text{Na}_8\text{Si}_{46}$	Pm-3n	10.1943(1)	10.2050(3)
$\text{Na}_x\text{Si}_{136}$	Fd-3m		14.6581(1)
Si	Fd3-m	5.4248(1)	5.4418(2)
	χ^2	4.78	4.17