Supplementary Information (SI) for Journal of Materials Chemistry A.

Supporting Information

Turning Residual Chlorides into Exfoliation Agents: Fully Gas-Phase Exfoliation of Silicon Nanosheets via Amine-Driven Expansion for Lithium-Ion Batteries

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Table S1. Weight change of SiNS during adsorption and desorption stages of NH_3 exfoliation. The corresponding molar ratio of NH_3 to $CaCl_2$ was calculated using Equation S1

Sample	Cycle	Stage	Weight Before (g)	Weight After (g)	x (xNH_3•$CaCl_2$)
SiNSh	1	Adsorption	3.89	5.17	3.61
		Desorption	4.34	3.31	0.16
	2	Adsorption	2.63	3.68	4.55
		Desorption	3.33	2.43	0.39
	3	Adsorption	1.74	2.48	5.17
		Desorption	2.23	1.70	1.31
SiNS	1	Adsorption	3.74	4.86	3.25 (3h); 3.62 (12h)
		Desorption	4.68	3.68	0.24
	2	Adsorption	2.86	3.74	3.66
		Desorption	3.48	2.64	0.14
	3	Adsorption	1.95	3.08	6.55
		Desorption	2.86	1.96	1.05

Note: Stage-wise sampling was performed using a separate batch to measure weight changes and tap density. The collection was carried out under Ar atmosphere, and the samples were immediately transferred into sealed plastic bags for measurement.

$$3CaSi_2 + 6HCl \rightarrow 3CaCl_2 + Si_6H_6 \qquad \text{(Equation 1)}$$

$$3CaSi_2 + 2AlCl3_3 \rightarrow 3CaCl_2 + 2Al + 6Si \qquad \text{(Equation 2)}$$

$$x_i = x_{i-1} + \frac{(Weight\ after\ - Weight\ Before)/MW_{NH3}}{Weight\ before\ \times conversion\ \times \dfrac{m_{CaCl2}}{m_{product} + x_{i-1} \times MW_{NH3}}}$$

(Equation S1)

Where x_i is amount adsorbed NH_3 per mole $CaCl_2$ (xNH_3•$CaCl_2$) at the *i*-th exfoliation stage. Weight after and weight before are the sample weight measurements immediately after and prior to an exfoliation stage, respectively. Conversion denotes the reaction conversion rate, typically set to 100% due to the near-complete reaction observed in the experiments. m_{CaCl2} is the theoretical mass of $CaCl_2$ produced per mole $CaSi_2$, and $m_{product}$ is the theoretical mass of all the products per mole $CaSi_2$.

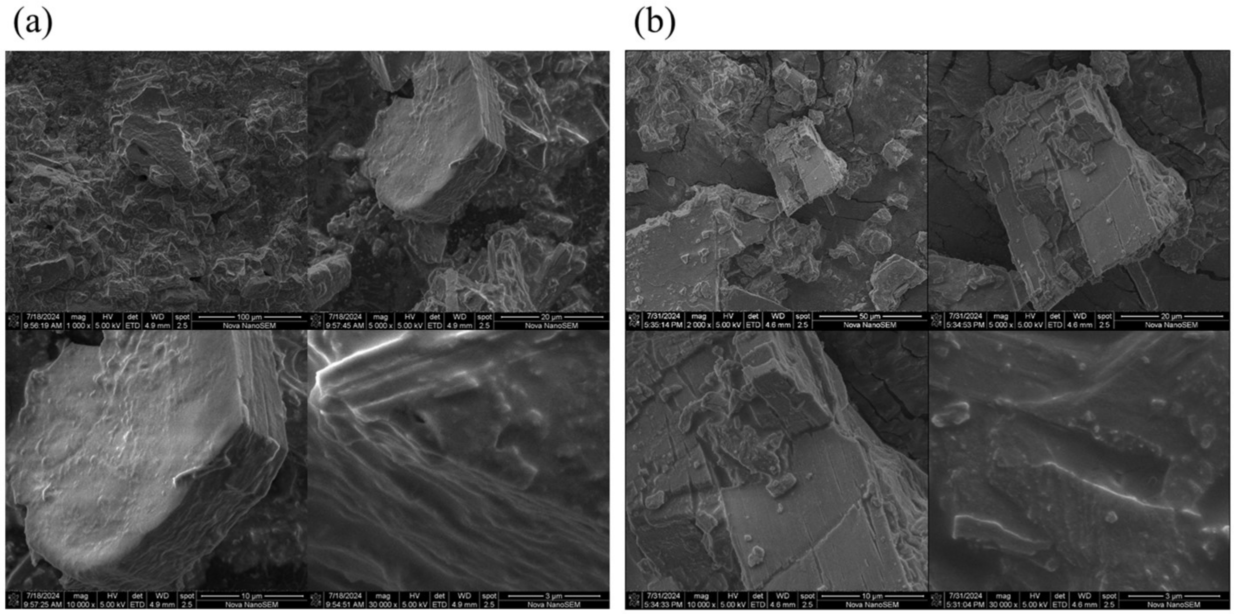

Figure S1. SEM images of (a) as-reacted SiNSh from the $CaSi_2$ gas phase reaction with HCl from PVC decomposition and (b) as-reacted SiNS from the same reaction but with 10% by mol reaction $AlCl_3$ at varying magnifications

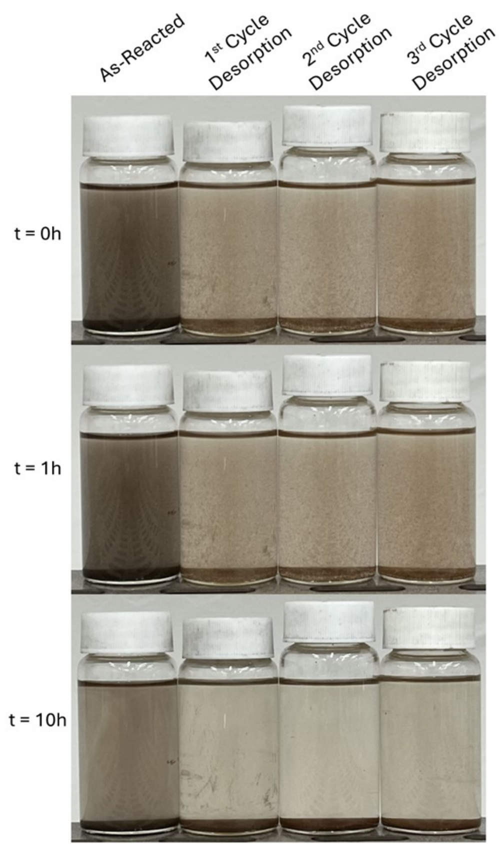

Figure S2. SEM images of (a) as-reacted SiNSh from the gas-phase reaction of $CaSi_2$ with HCl derived from PVC decomposition and (b) as-reacted SiNS from the same reaction but with 10 mol% $AlCl_3$ added, shown at varying magnifications

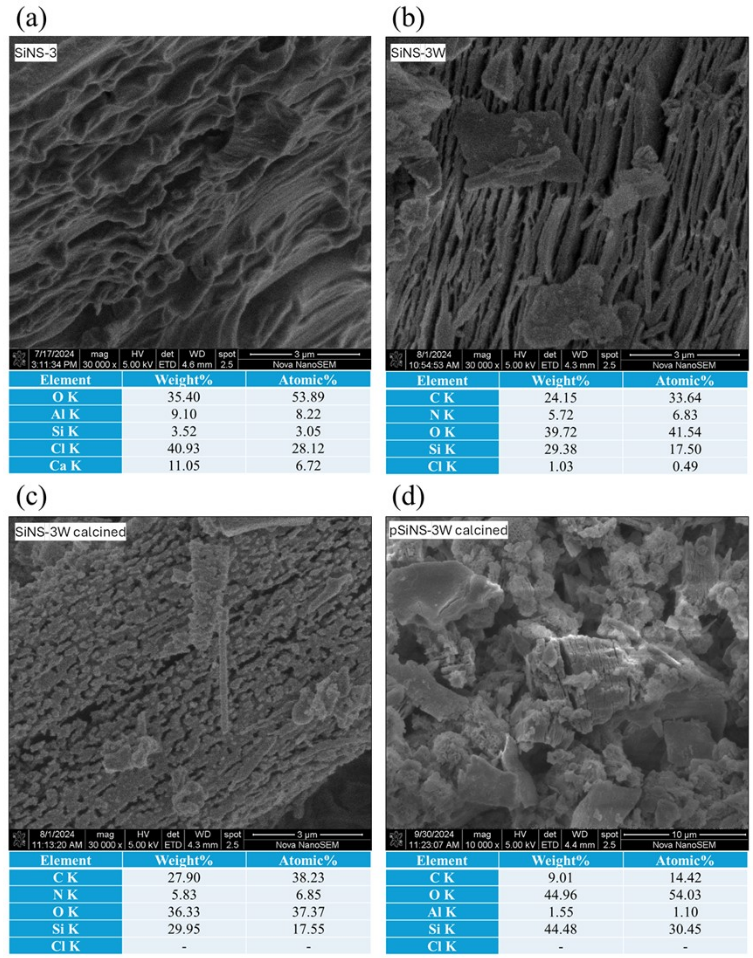

Figure S3. SEM and EDS analysis of (a) exfoliated SiNS-3, (b) washed SiNS-3W, (c) calcined SiNS-3W, and (d) pre-oxidized pSiNS-3W after calcination.

Table S2. Brunauer-Emmett-Teller (BET) specific surface area and mesopore average pore size analysis of as-reacted SiNS and NH_3-exfoliated SiNS with varying exfoliation cycles

Exfoliation Cycles	SiNS	SiNS-1	SiNS-2	SiNS-3	SiNS-5
BET Surface Area (m^2/g)	2.5239 ± 0.0316	69.5194 ± 0.1639	91.6700 ± 0.5297	134.8704 ± 0.5007	161.1239 ± 0.9299
Langmuir Surface Area (m^2/g)	3.4365 ± 0.0293	94.6111 ± 1.6989	126.4156 ± 1.8380	187.9204 ± 3.4235	220.9740 ± 3.3129
Adsorption average pore width (4V/A by BET)(Å)	68.797	94.0857	86.2988	84.7528	64.2168
BJH Adsorption average pore diameter (4V/A)(Å)	275.8606	193.5952	159.5689	128.678	124.1932
BJH Desorption average pore diameter (4V/A)(Å)	221.3573	151.5688	117.8458	101.0053	108.8064

Table S3. Summary of recent literature on the electrochemical performance of two-dimensional silicon nanosheets as LIB anode materials.

Work	2D Material	Specific Current *$A\ g^{-1}$*	Specific Capacity *$mAh\ g^{-1}$*	ICE	Reversible Capacity *$mAh\ g^{-1}$ (cycle)*
This Work	**Si NS**	**2.0**	**1708**	**78%**	**873 (500^{th})**
Xie (2022) [1]	SiOx/C-Ag NS	0.6	1477	65.4%	550 (500^{th})
Dong (2024) [2]	Si NS@SiOx/C	1.0	1561	63.1	659.3 (500^{th})
Kumar (2020) [3]	Si NS/G	0.2	1480	78%	1040 (1000^{th})
Wang (2023) [4]	Si NS@C (h/s/h)	4.0	1250	86%	994 (1000^{th})
Sun (2024) [5]	pSi@C	1.0	1000	94%	549 (1000^{th})
Gao (2024) [6]	Si NS@C	0.5	2750	66%	300 (300^{th})
Wan (2023) [7]	Si NS/C	1.0	950	55.7%	869 (300^{th})
Hou (2022) [8]	Si NS	1.0	1800	79%	1300 (300^{th})
Lau (2025) [9]	Si NS	2.0	2616	87.7%	1230 (200^{th})
Sun (2022) [10]	Si NS/SiOx/C	0.1	2067	61.3%	1400 (200^{th})
Liu (2023) [11]	Si NS	2.0	2390	64.2%	1115 (200^{th})
Dong (2022) [12]	B-doped Si NS	2.0	800	81%	842 (200^{th})
Lee (2024) [13]	Si NS/PI	0.3	1809	42.4%	585 (200^{th})
Yang (2024) [14]	Si NS@C-Fe_3O_4	1.0	1834	41%	857 (200^{th})

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