SUPPORTING INFORMATION

Stabilizing Effects of Phosphorus-Doped Silicon Nanoparticle Anodes in Lithium-Ion Batteries

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S1. Materials Naming Convention

Table S1. Naming convention for SiP_x materials based on synthesis protocol employed.

Synthetic Parameter Varied	Nominal P Content (at%)	Ramp Rate (°C min^{-1})	Temperature Setpoint (°C)	Hold Time (h)	Material
Control Si	0	(none)	(none)	(none)	Si (100 nm)
	0	(none)	(none)	(none)	Si (500 nm)
	0	(none)	(none)	(none)	Si (44 μm)
	0	5	1131	1	**0.0P**-5R-H-1h
P Content	0.05	5	1131	1	**0.05P**-5R-H-1h
	0.1	5	1131	1	**0.1P**-5R-H-1h
	0.2	5	1131	1	**0.2P**-5R-H-1h
	1.0	5	1131	1	**1.0P**-5R-H-1h
	3.0	5	1131	1	**3.0P**-5R-H-1h
Ramp Rate	0.1	5	1131	0	0.1P-**5R**-H-0h
	0.1	10	1131	0	0.1P-**10R**-H-0h
	0.1	20	1131	0	0.1P-**20R**-H-0h
	0.1	30	1131	0	0.1P-**30R**-H-0h
	0.1	50	1131	0	0.1P-**50R**-H-0h
Temperature	0.1	5	1131	1	0.1P-5R-**H-1h**
	0.1	5	1131	0	0.1P-5R-**H-0h**
	0.1	5	800	1	0.1P-5R-**L-1h**
	0.1	5	800	0	0.1P-5R-**L-0h**
Hold Time	0.1	5	1131	0	0.1P-5R-H-**0h**
	0.1	5	1131	1	0.1P-5R-H-**1h**
	0.1	5	1131	6	0.1P-5R-H-**6h**
	0.1	5	1131	12	0.1P-5R-H-**12h**

S2. Color as a Function of P-Doping

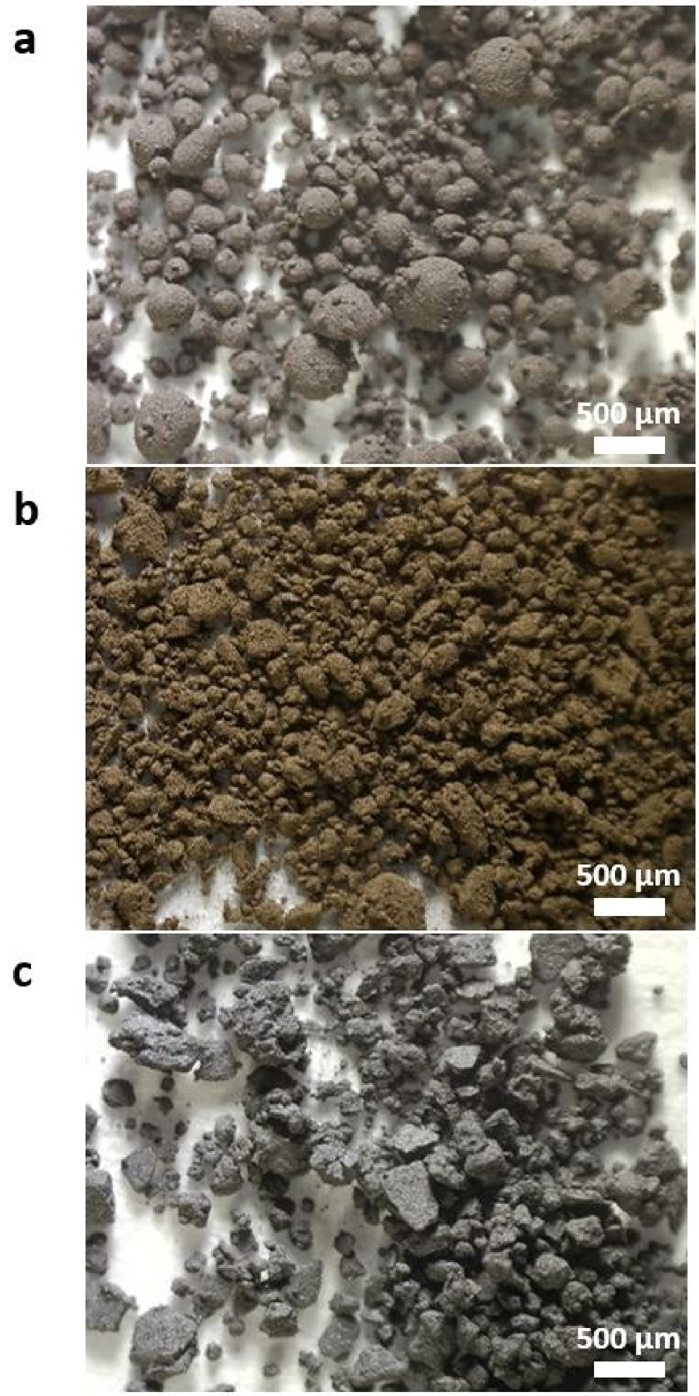

Figure S1. Photographs of (a) as-received pure Si, (b) 0.1 at% SiP_x, and (c) 3.0 at% SiP_x, all obtained from the same precursor: 500 nm Si NPs.

S3. Raman Spectroscopy Variation as a Function of P-Doping

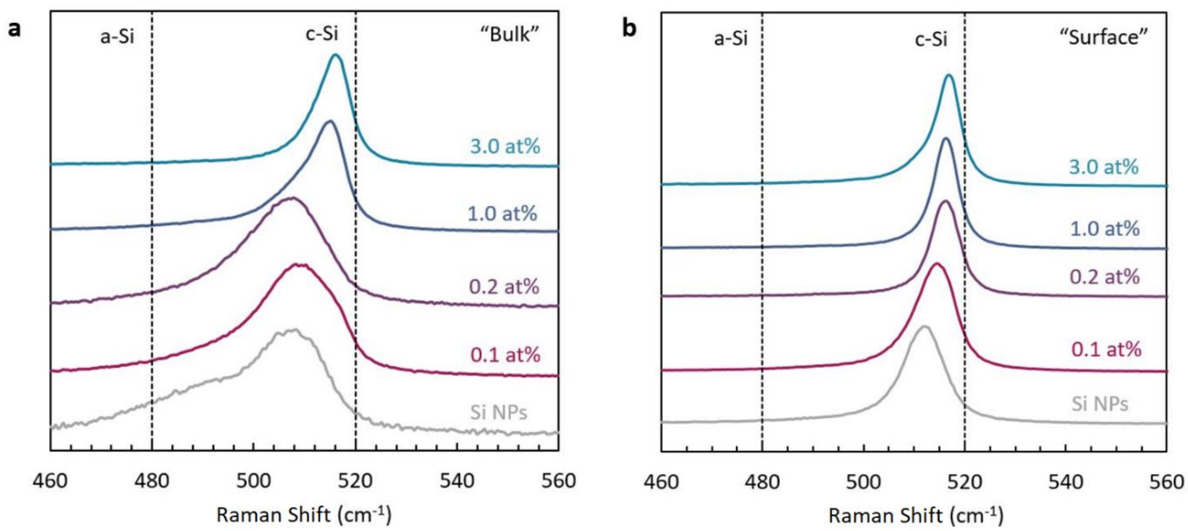

Figure S2. Raman spectroscopy of SiP_x NPs measured (a) within the powder bulk and (b) directly at the powder surface, using 532 nm incident radiation. All materials were obtained from the same precursor (500 nm Si NPs) under heating at 5 °C min^{-1}, holding at 1131 °C for 1 h.

S4. Crystallite Size as a Function of P-Doping

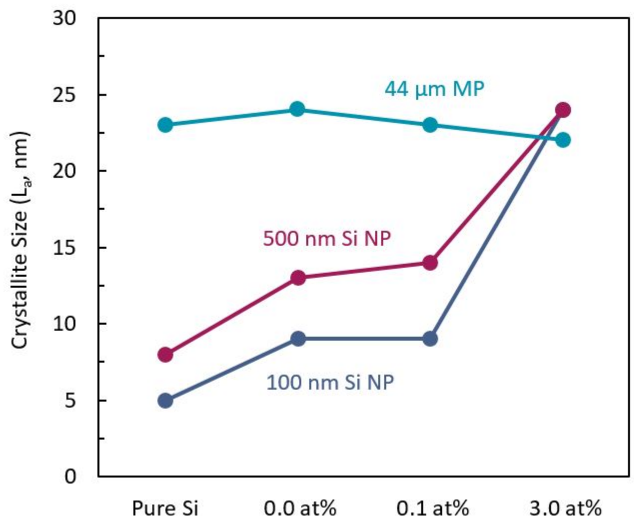

Figure S3. Crystallite size as a function of phosphorus doping shown for three different sized Si precursors (100 nm, 500 nm, and 44 µm). Si and SiP_x materials were treated under the following conditions: xxP-5R-H-1h.

S5. Raman Spectroscopy Variation of Heterogeneously Doped SiP_x

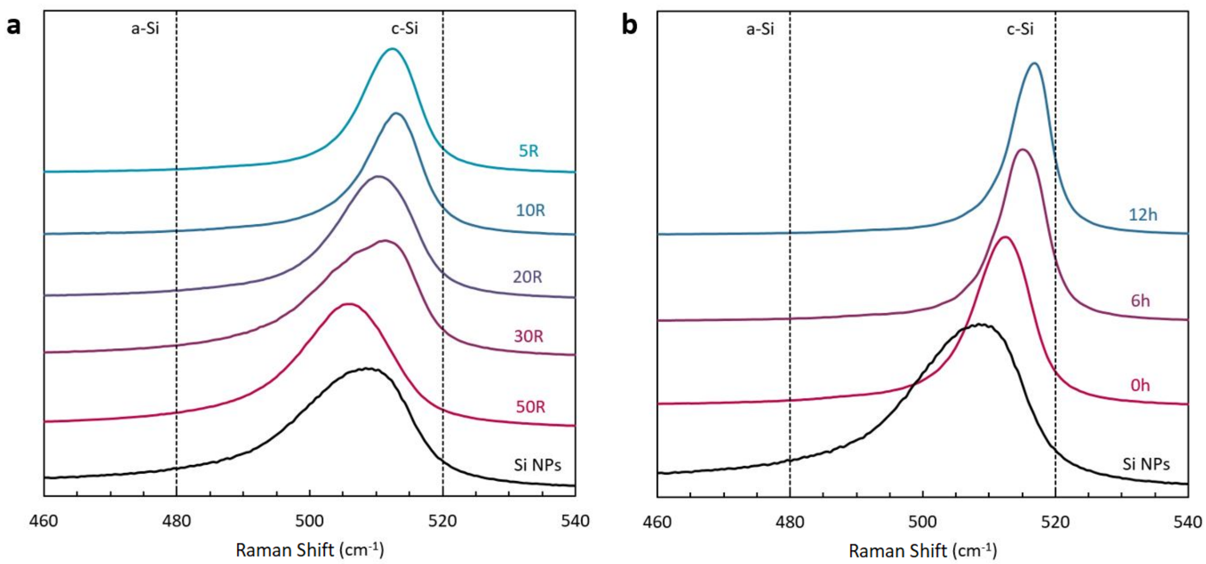

Figure S4. Raman spectroscopy of SiP_x NPs synthesized under (a) different ramp rates (0.1P-xxR-H-0h) and (b) different hold times (0.1P-5R-H-xxh), using 532 nm incident radiation. All materials were obtained from the same precursor (500 nm Si NPs).

S6. Capacity Retention of Pure Si NPs and MPs

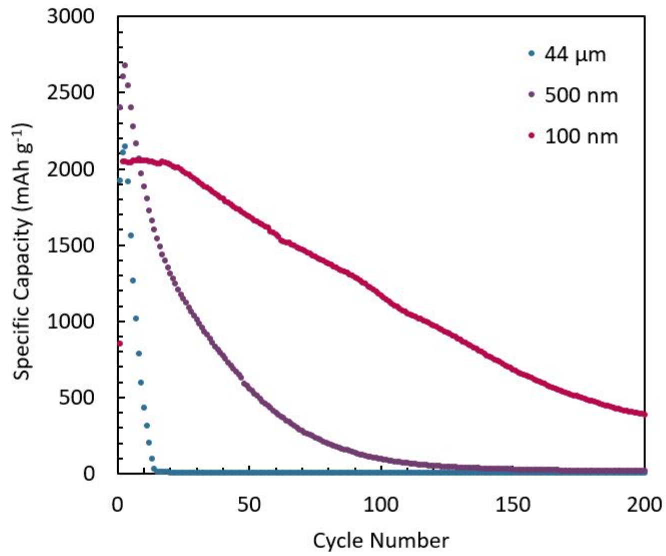

Figure S5. GCD capacity retention of pure as-received 100 nm, 500 nm, and 44 um Si NPs and MPs.

S7. Electrochemical Effects of High Temperature and Hold Time

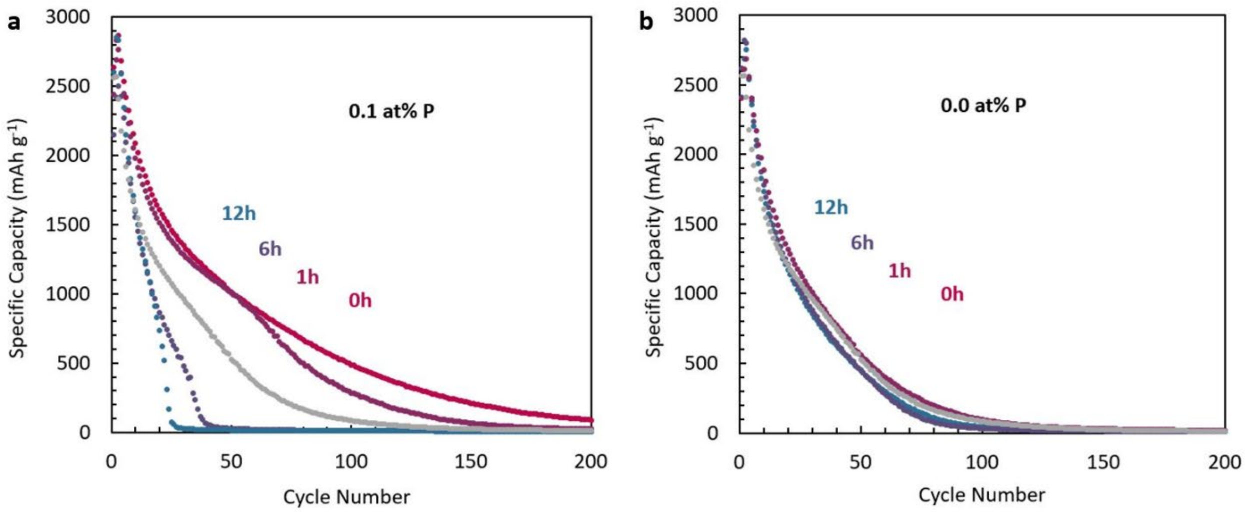

Figure S6. Capacity retention of a) 0.1 at% doped and b) undoped Si NPs at different hold times. All materials in (a-b) were obtained under heating at 5 °C min^{-1} and holding at 1131 °C.

S8. Crystallite Size as a Function of Hold Time at High Temperature

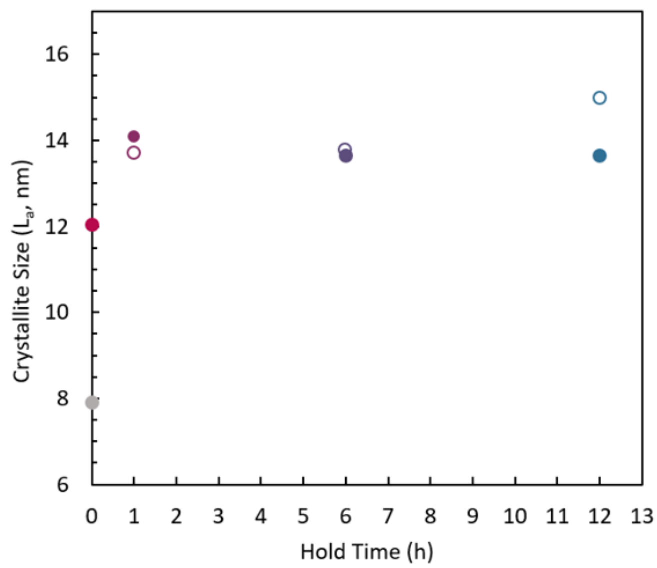

Figure S7. Crystallite size as a function of hold time (0, 1, 6, and 12 h) for undoped Si NPs (open circles) and 0.1 at% P doped Si NPs (closed circles) synthesized under the following conditions (0.1P-5R-H-xxh) . The closed grey circle is pure Si NP as received.

S9. Thermal Decomposition Temperature as a Function of P-Doping

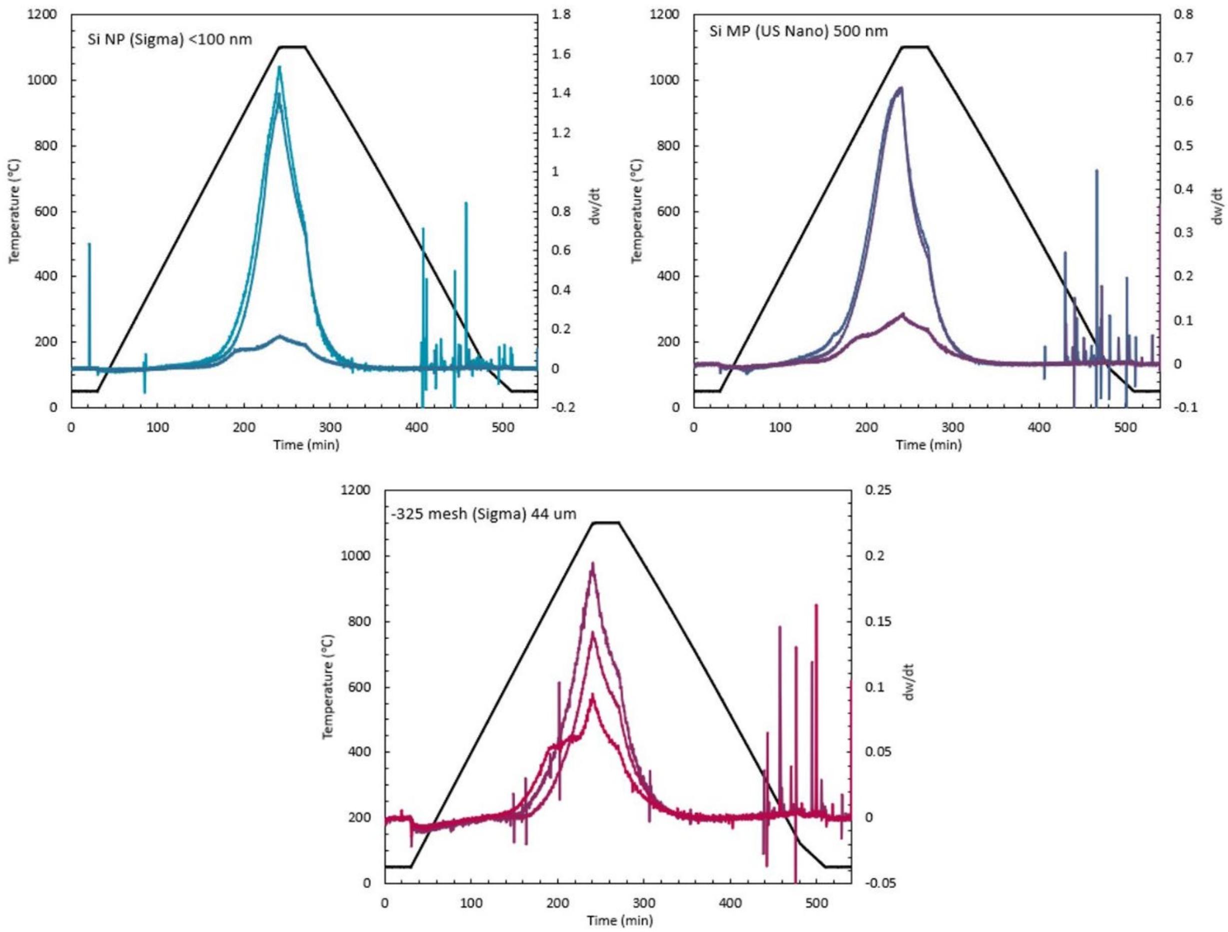

Figure S8. Differential TGA profiles for three series of SiP_x samples, based on three silicon precursors: (top left) 100 nm NPs, (top right) 500 nm NPs, and (bottom) 44 µm MPs. The compositions of the samples are 0 at%, 0.1 at%, and 3.0 at% P in Si, from lightest to darkest.