

**Zincothermic reduction of silica to silicon: Make the impossible possible**

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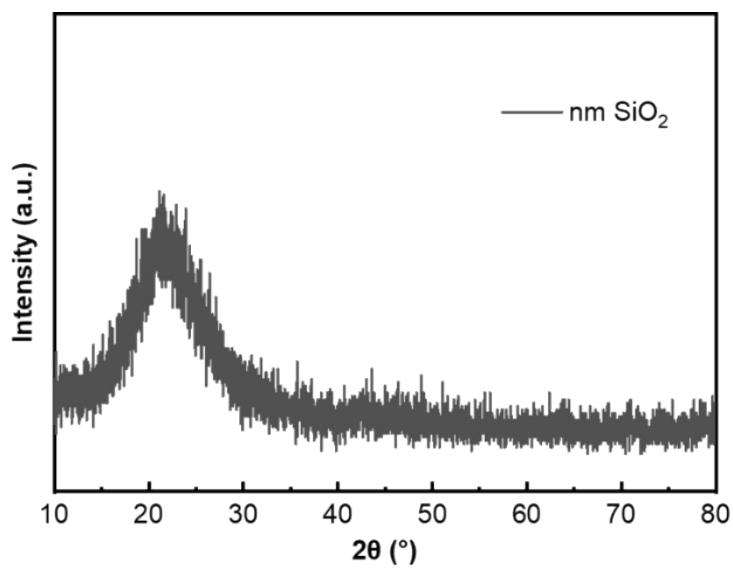


Fig. S1 The XRD pattern of nano-SiO<sub>2</sub> materials.

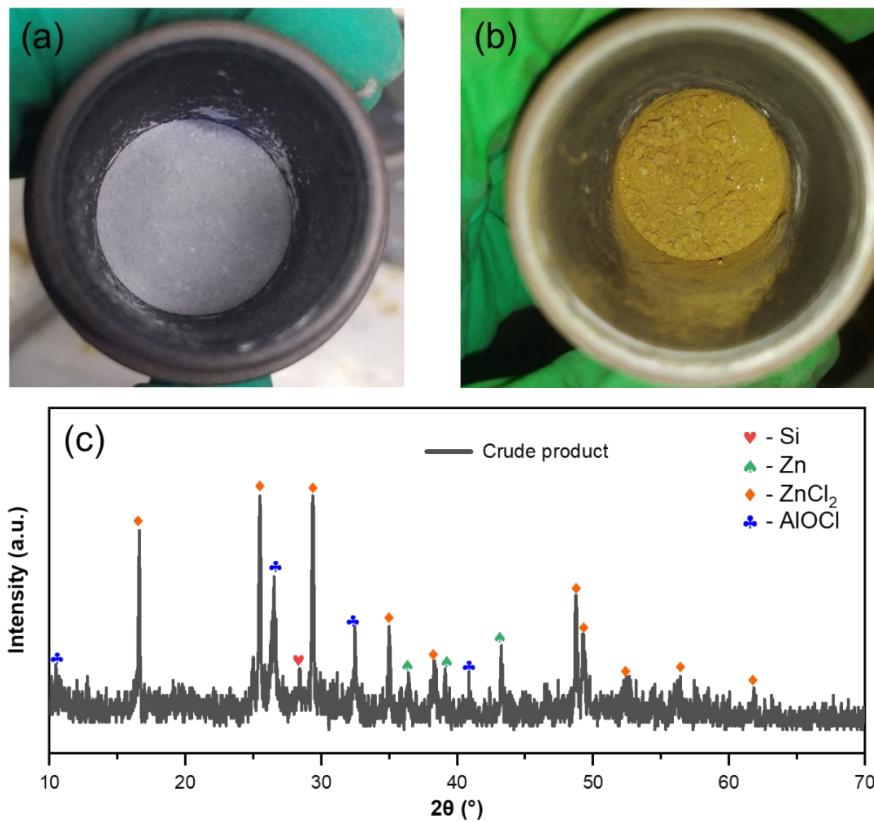


Fig. S2 Optical photograph of the (a) unreacted product including AlCl<sub>3</sub>+SiO<sub>2</sub>+Zn, (b) crude product obtained at 250 °C for 12 h without any treatment (contains salts), and (c) XRD pattern of the crude product.

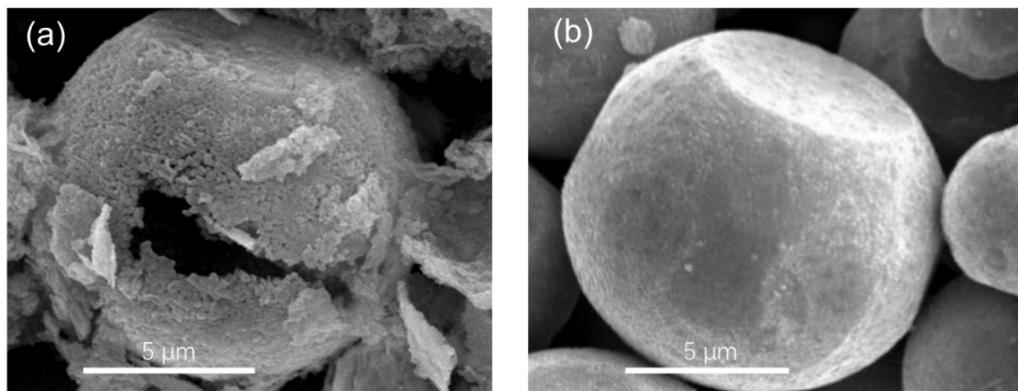


Fig. S3 SEM images of (a) hollow Si and (b) its corresponding reducing agent micro Zn particle.

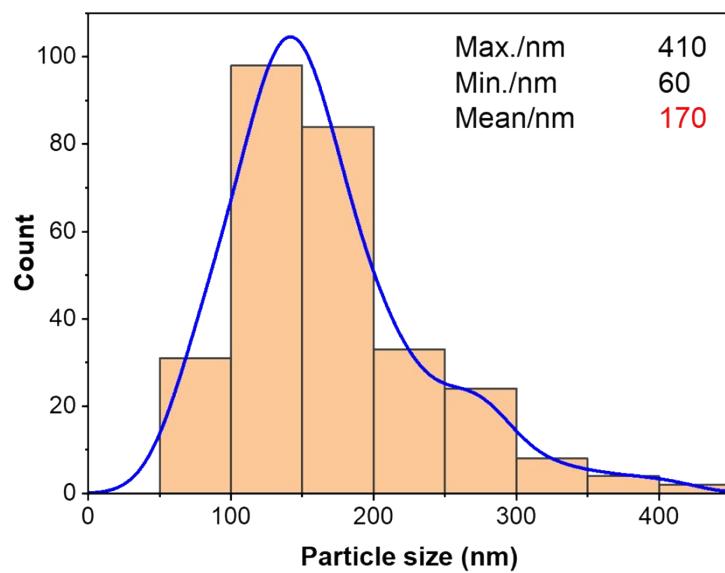


Fig. S4 Distribution profile of Si nanoparticle sizes from ZnR-Si after 10 minutes of manual grinding.

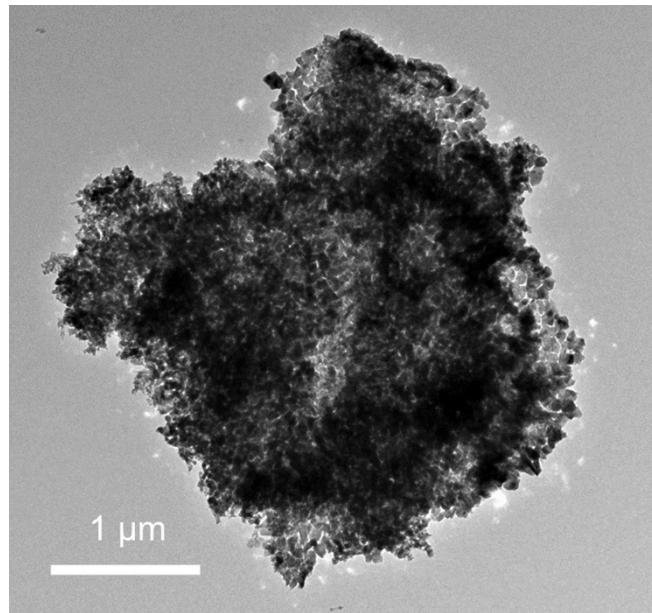


Fig. S5. TEM images of ZnR-Si with similar hollow structures and the hollow Si shell made by nano Si particles.

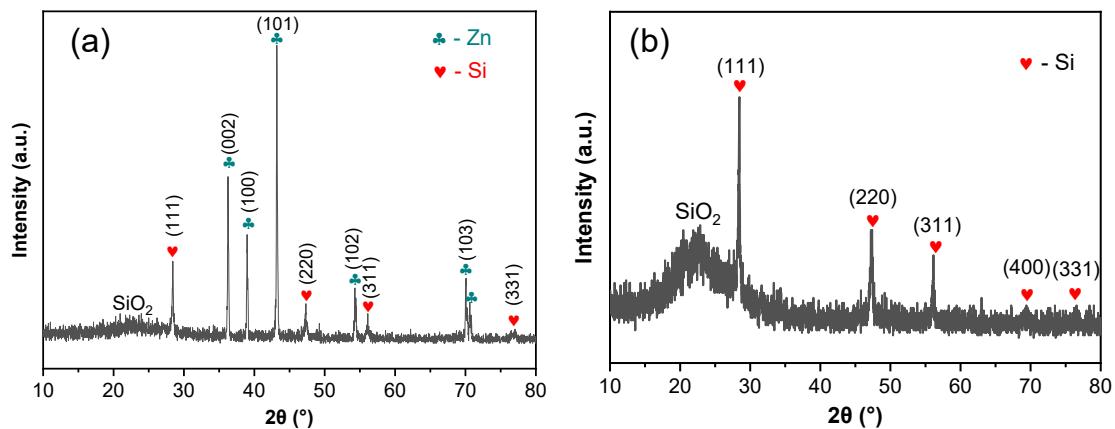


Fig. S6 XRD patterns of the zincothermic reduction sample (a) after 3 times of water washing, (b) after HCl and water washing (no HF leaching).

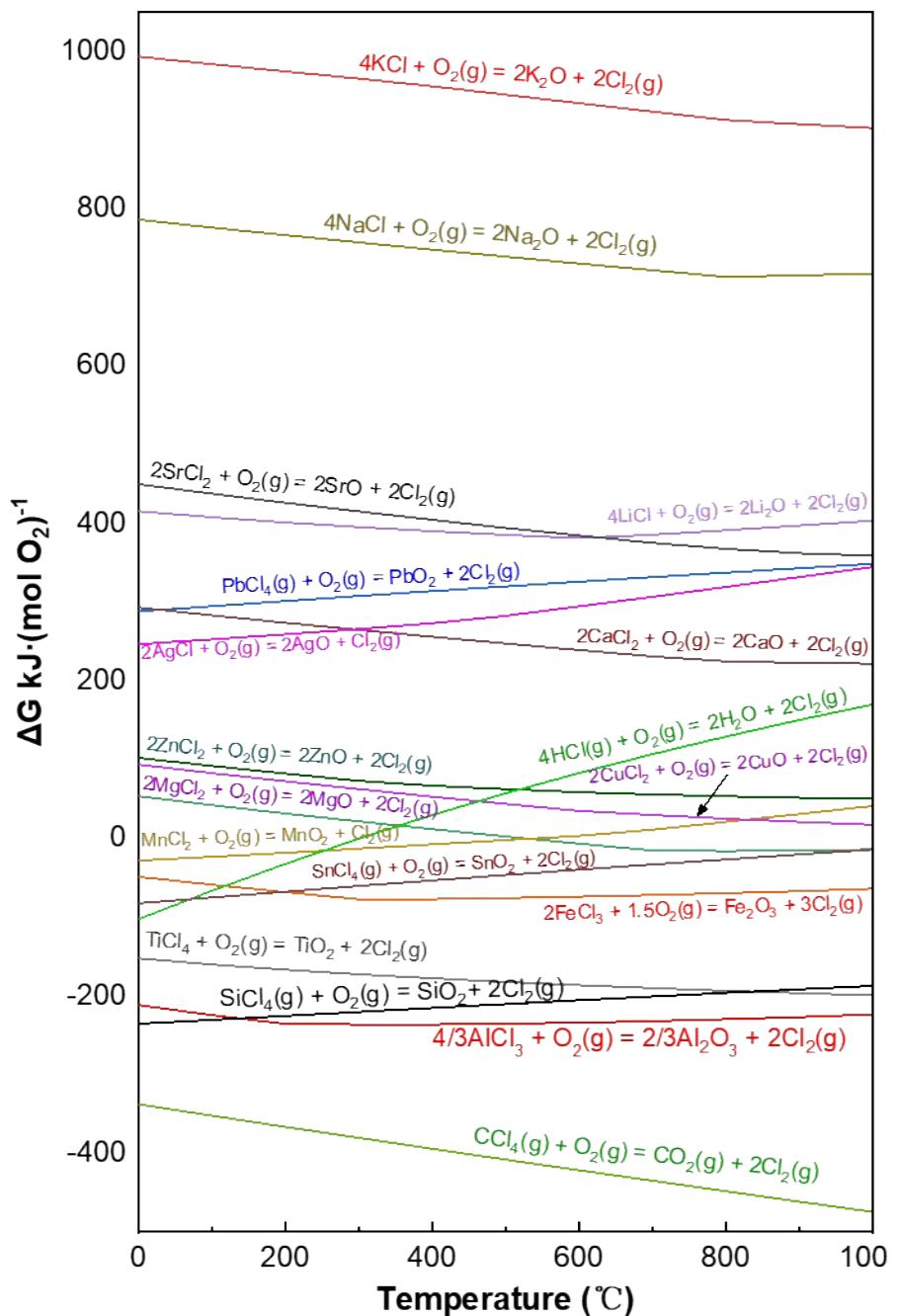


Fig. S7 Gibbs free energy profiles of the reaction of typical chlorides with oxygen as a function of temperature.

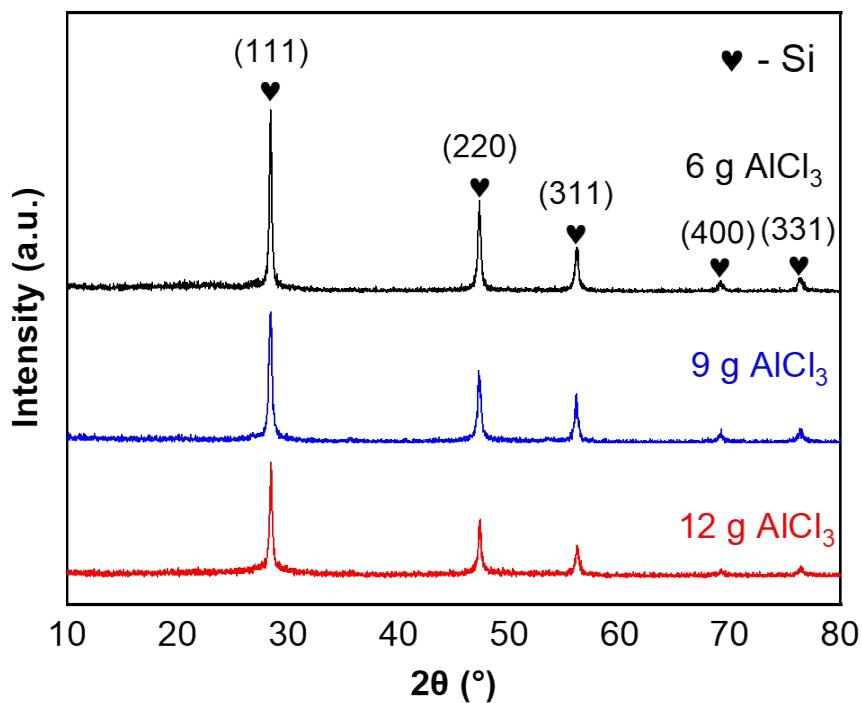


Fig. S8 XRD patterns of ZnR-Si samples with different  $\text{AlCl}_3$  contents at 250 °C 12 h.

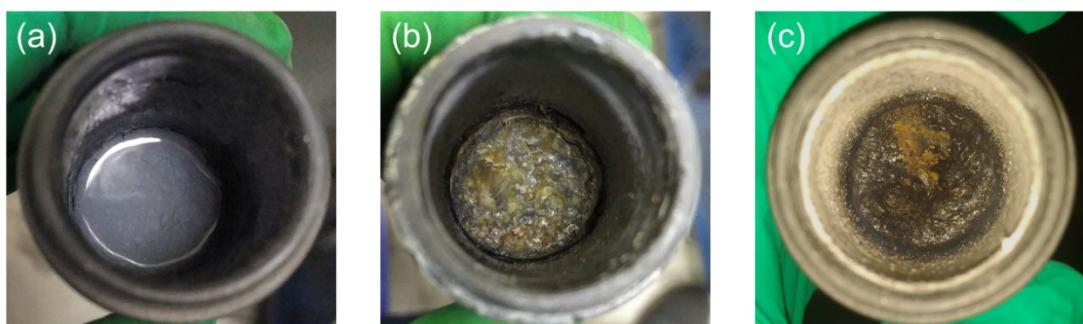


Fig. S9 Optical photographs of micro Zn powder (3 g) mixed with  $\text{SiCl}_4$  solution (2.8 g) after reaction without any treatment. (a) The sample without  $\text{AlCl}_3$  salt obtained at 250 °C 24 h, (b) added 2 g  $\text{AlCl}_3$  obtained at 250 °C for 12 h, (c) added 5 g  $\text{AlCl}_3$  obtained at 250 °C for 12 h.

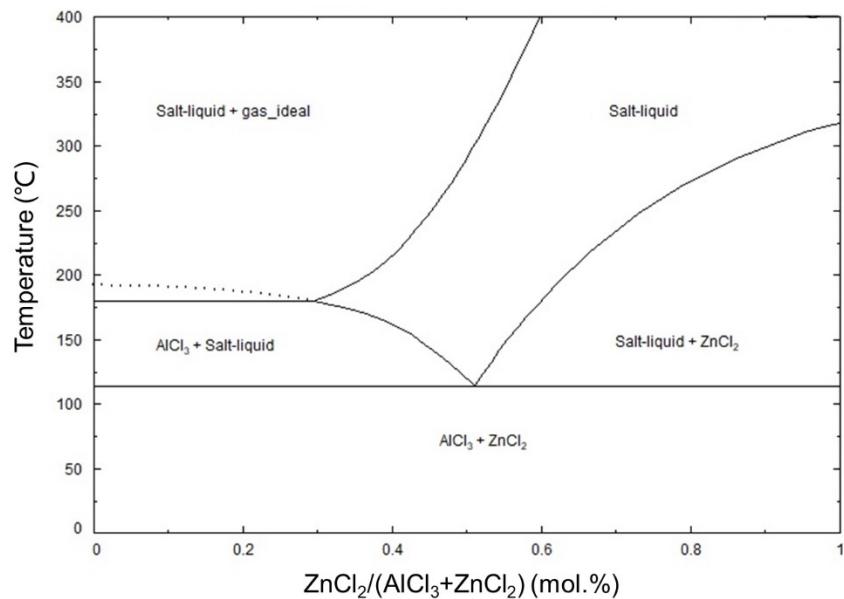


Fig. S10 Phase diagram of AlCl<sub>3</sub>-ZnCl<sub>2</sub> binary system<sup>1</sup>.

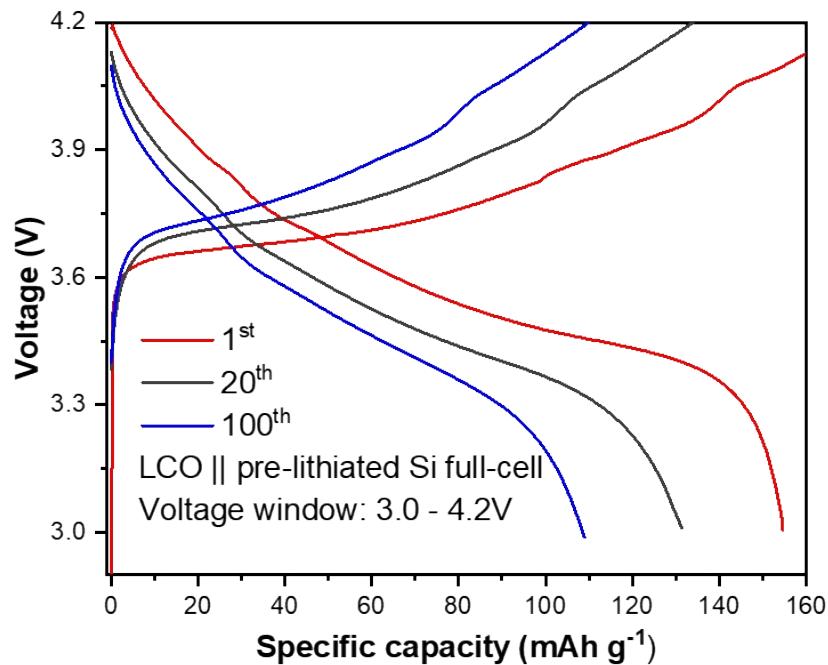


Fig. S11 Charge/discharge profiles of the LCO||Pre-lithiated Si full-cell at the 1<sup>st</sup>, 20<sup>th</sup>, and 100<sup>th</sup> cycles.

Table S1. Methods of producing silicon under various temperatures and with different reducing agents.

Si source	Reducing agent	Reducing Temperature (°C)	Reducing Time (h)	Synthesis conditions	Structure	Ref.
SiO <sub>2</sub>	C	1724 ~ 1990	n/a	Vacuum	Bulk Si	<sup>2</sup>
SiO <sub>2</sub>	C	1500–2000	n/a	n/a	Bulk Si	<sup>3</sup>
quartz	electron	850	1	Molten CaCl <sub>2</sub> based salt	Nano rods	<sup>4</sup>
MgSiO <sub>3</sub>	electron	650	12	Molten MgCl <sub>2</sub> based salt	Nano particles	<sup>5</sup>
SiCl <sub>4</sub>	electron	850	n/a	Molten KF-KCl	Bulk Si	<sup>6</sup>
SiO <sub>2</sub>	Al	700	4	n/a	Macro porous	<sup>7</sup>
Rice husks	Al	700	3	n/a	Porous SiO <sub>x</sub> @C	<sup>8</sup>
SiO <sub>2</sub>	Mg	650	2.5	n/a	Micro porous	<sup>9</sup>
SiO <sub>2</sub>	Mg	650	2.5	Solid NaCl	Nano porous	<sup>10</sup>
SiO <sub>2</sub>	Al or Mg	250	12	Molten AlCl <sub>3</sub>	Nano spheres	<sup>11</sup>
SiO <sub>2</sub> @C	Al	300	12	Molten AlCl <sub>3</sub> -NaCl	Nano Si@C	<sup>12</sup>
SiO <sub>2</sub> @C	Al	220	16	Molten AlCl <sub>3</sub> -ZnCl <sub>2</sub>	Micro Si@C	<sup>13</sup>
SiCl <sub>4</sub>	Mg	200	10	Molten AlCl <sub>3</sub>	Nano particles	<sup>14</sup>
SiO <sub>2</sub>	Zn	250	12	Molten AlCl <sub>3</sub>	Hollow spheres	This work

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