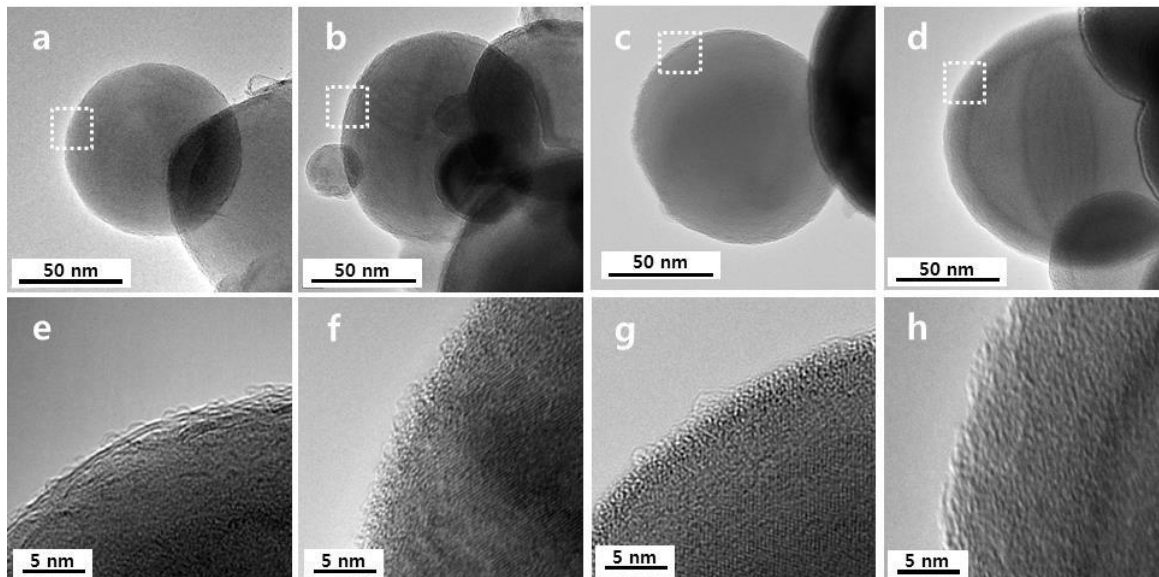
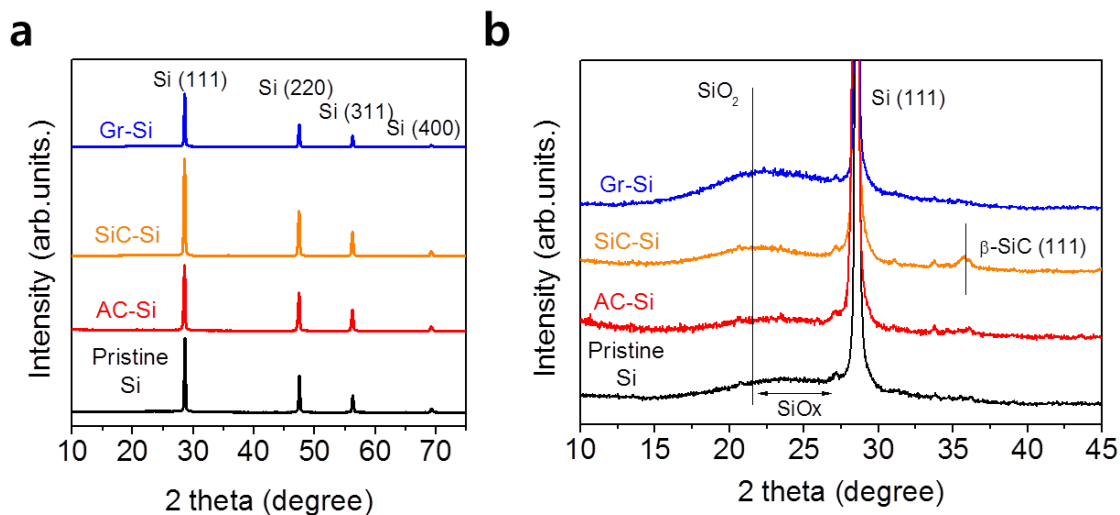


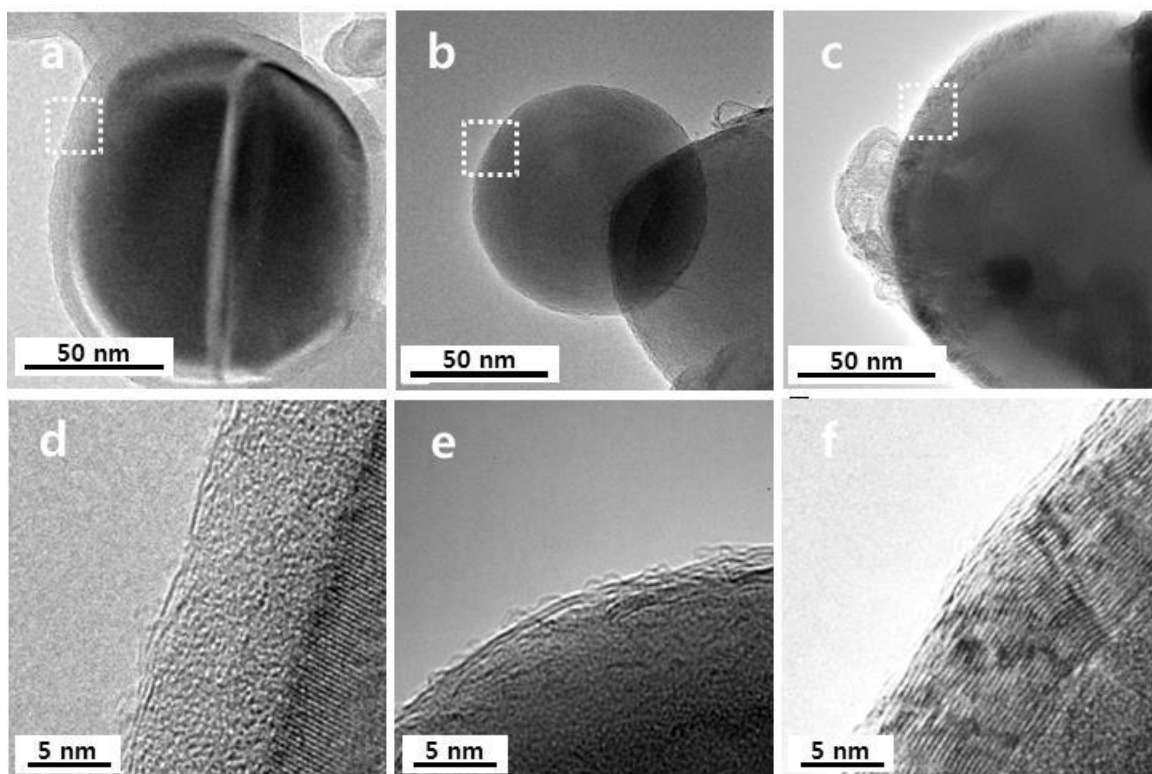
Supplementary Figures



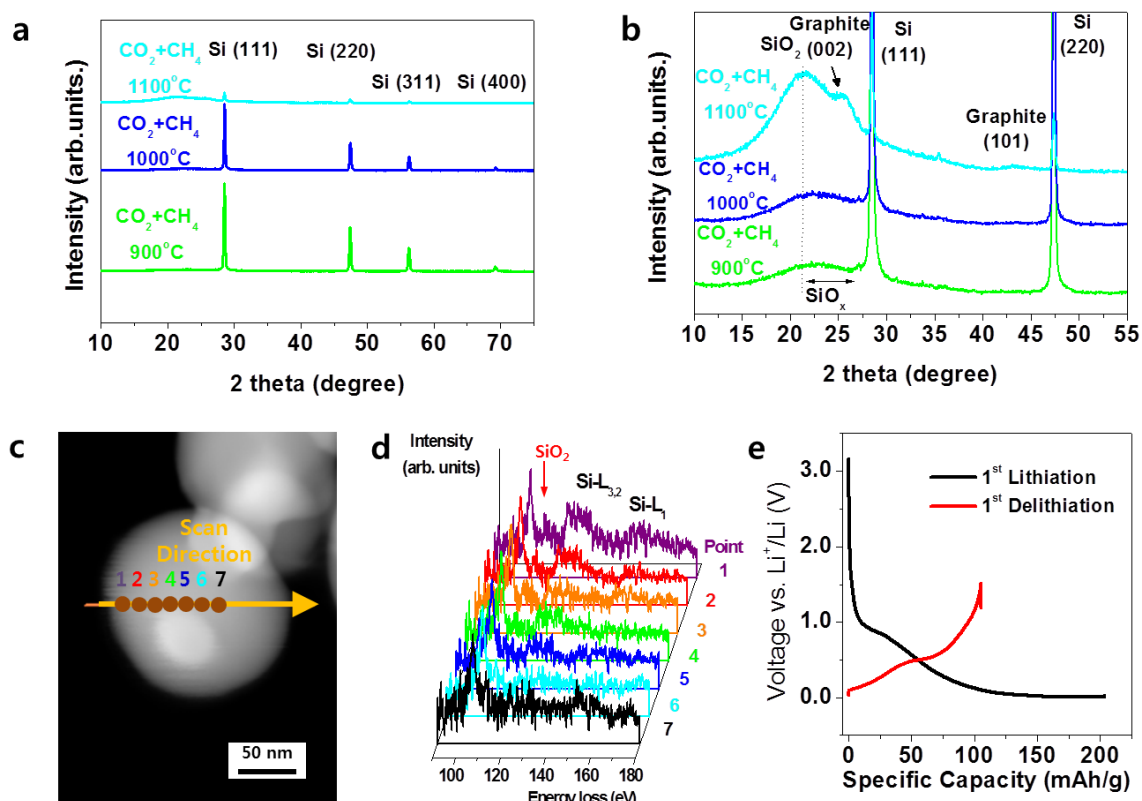
Supplementary Figure 1. TEM characterization of the Si active particles used in this study. Low and high magnification TEM images of **(a,e)** Gr-Si (CO₂ + CH₄, 1000 °C), **(b,f)** SiC-Si (H₂ + CH₄, 1000 °C), **(c,g)** AC-Si (citric acid, 400 °C), and **(d,h)** pristine Si.



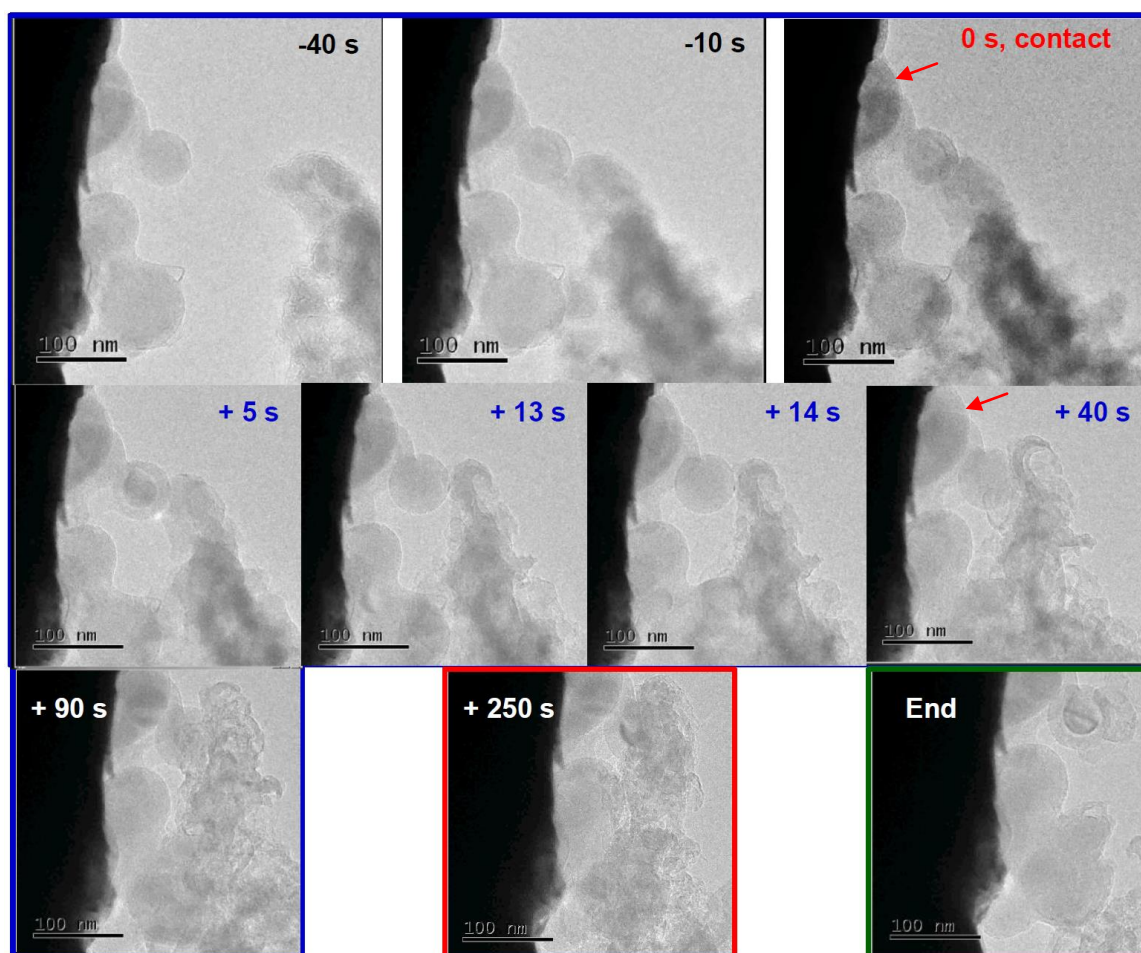
Supplementary Figure 2. XRD analysis of different Si NPs. XRD spectra of Gr-Si (synthesized at 1000 °C), SiC-Si, AC-Si, and pristine Si in (a) wide and (b) small 2θ ranges. While SiC-Si shows a signal of $\beta\text{-SiC}$ at 35.8°, Gr-Si exhibits no such peak confirming its SiC-free synthesis. Gr-Si also shows a broad peak around 22° indicating remaining SiO_2 surface layer.



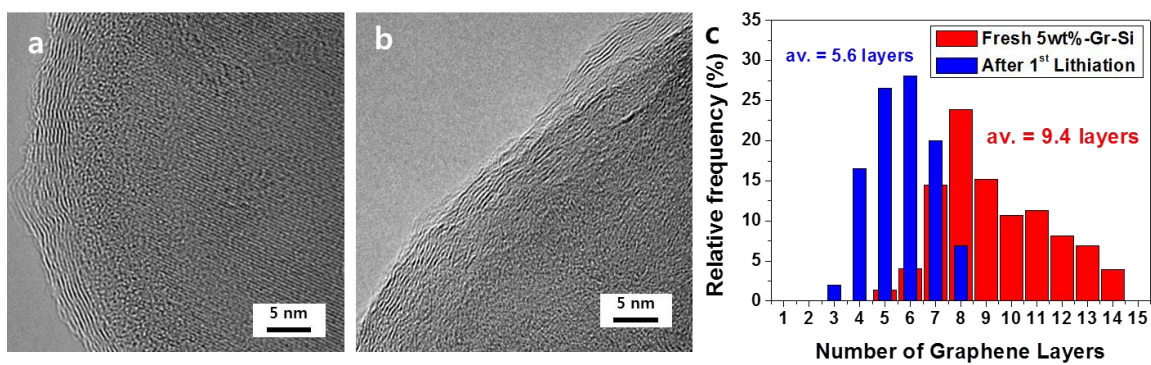
Supplementary Figure 3. TEM characterization of Gr-Si synthesized at different temperatures. Low and high magnification TEM images of Gr-Si synthesized at (a,d) 900 °C, (b,e) 1000 °C and (c,f) 1100 °C.



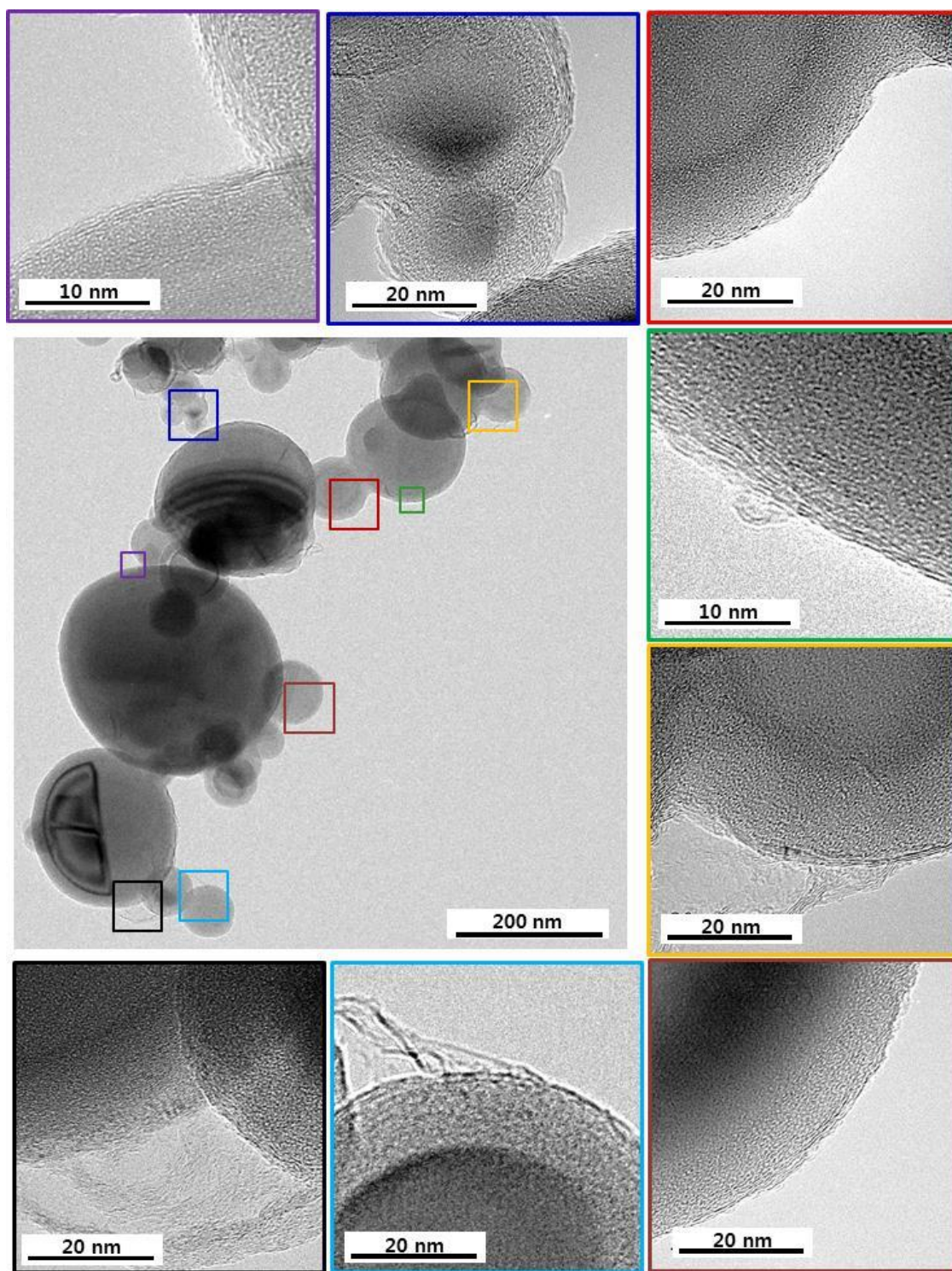
Supplementary Figure 4. Characterizations of Gr-Si synthesized at different temperatures. XRD spectra of Gr-Si NPs synthesized at 900, 1000 and 1100 °C in (a) wide and (b) small 2 theta ranges. (c) A STEM image of a Gr-Si NP synthesized at 1100 °C. (d) EELS spectra for the spots denoted in (c). (e) The first lithiation-delithiation profile of a half-cell based on Gr-Si synthesized at 1100 °C.



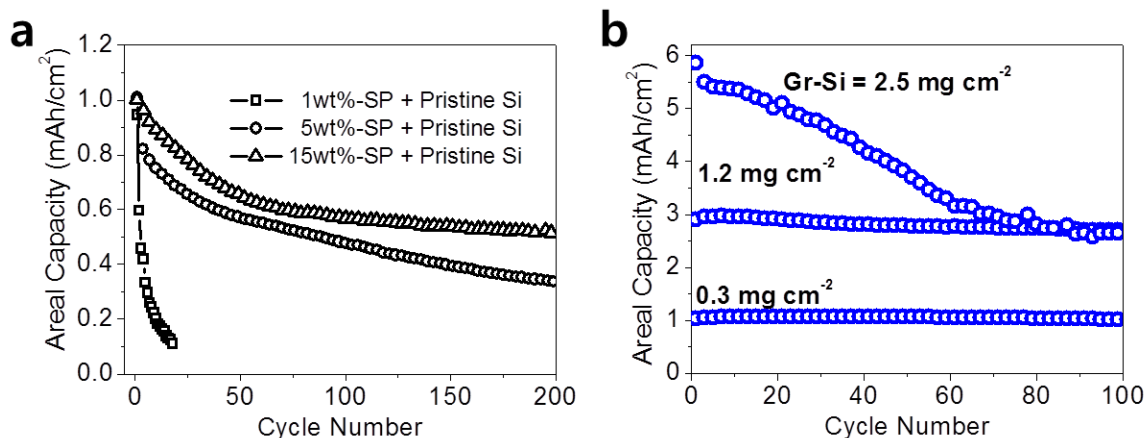
Supplementary Figure 5. *In-situ* TEM analysis. Screen capture images of Supplementary Movie 1 (blue line), Supplementary Movie 2 (red line), and Supplementary Movie 3 (green line).



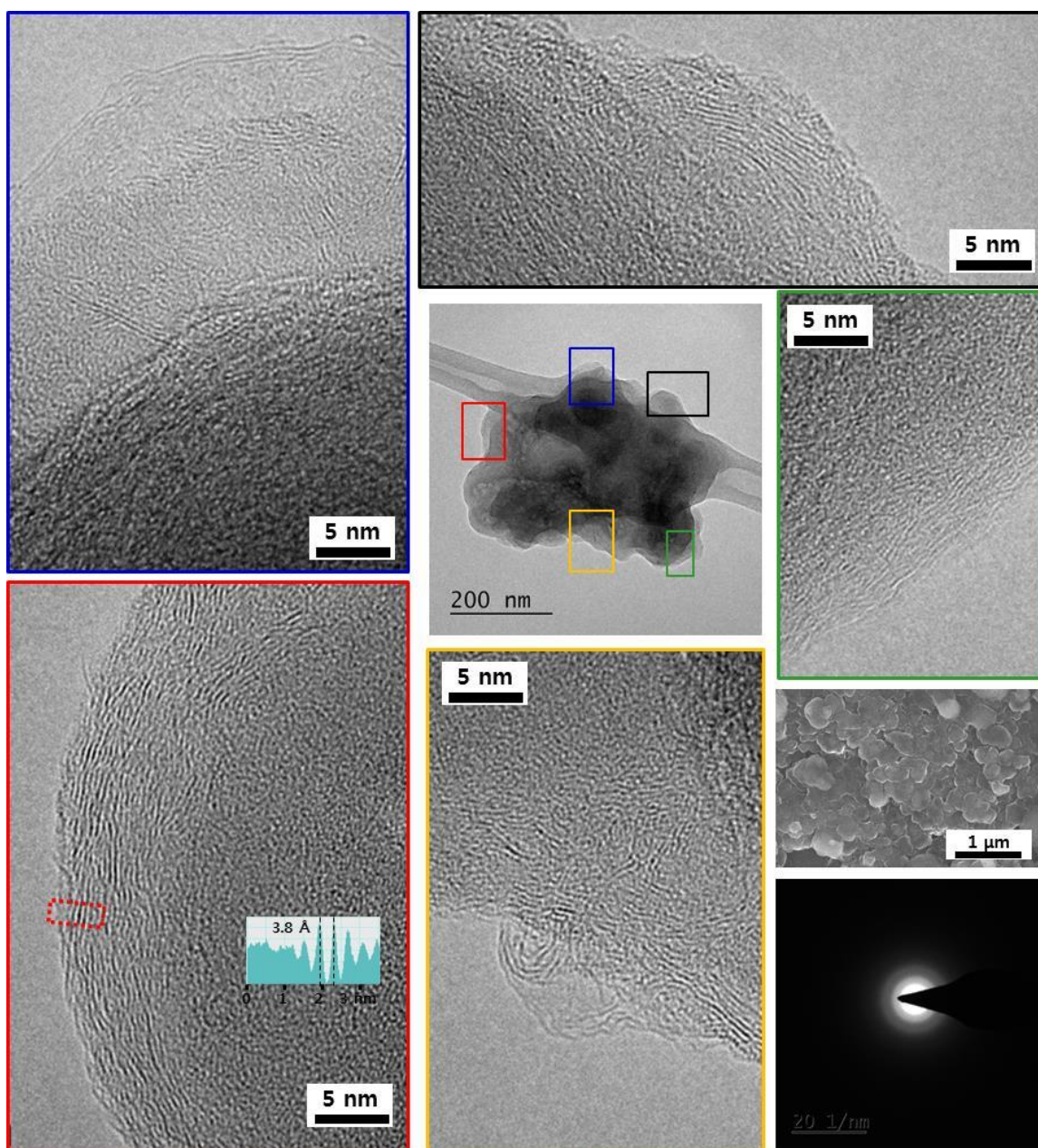
Supplementary Figure 6. *Ex-situ* TEM analysis of Gr-Si NPs before and after the 1st lithiation. Close up TEM images of 5wt%-Gr-Si NP (a) before and (b) after the 1st lithiation. (c) Statistics on the number of graphene layers on Si surface before and after the 1st lithiation.



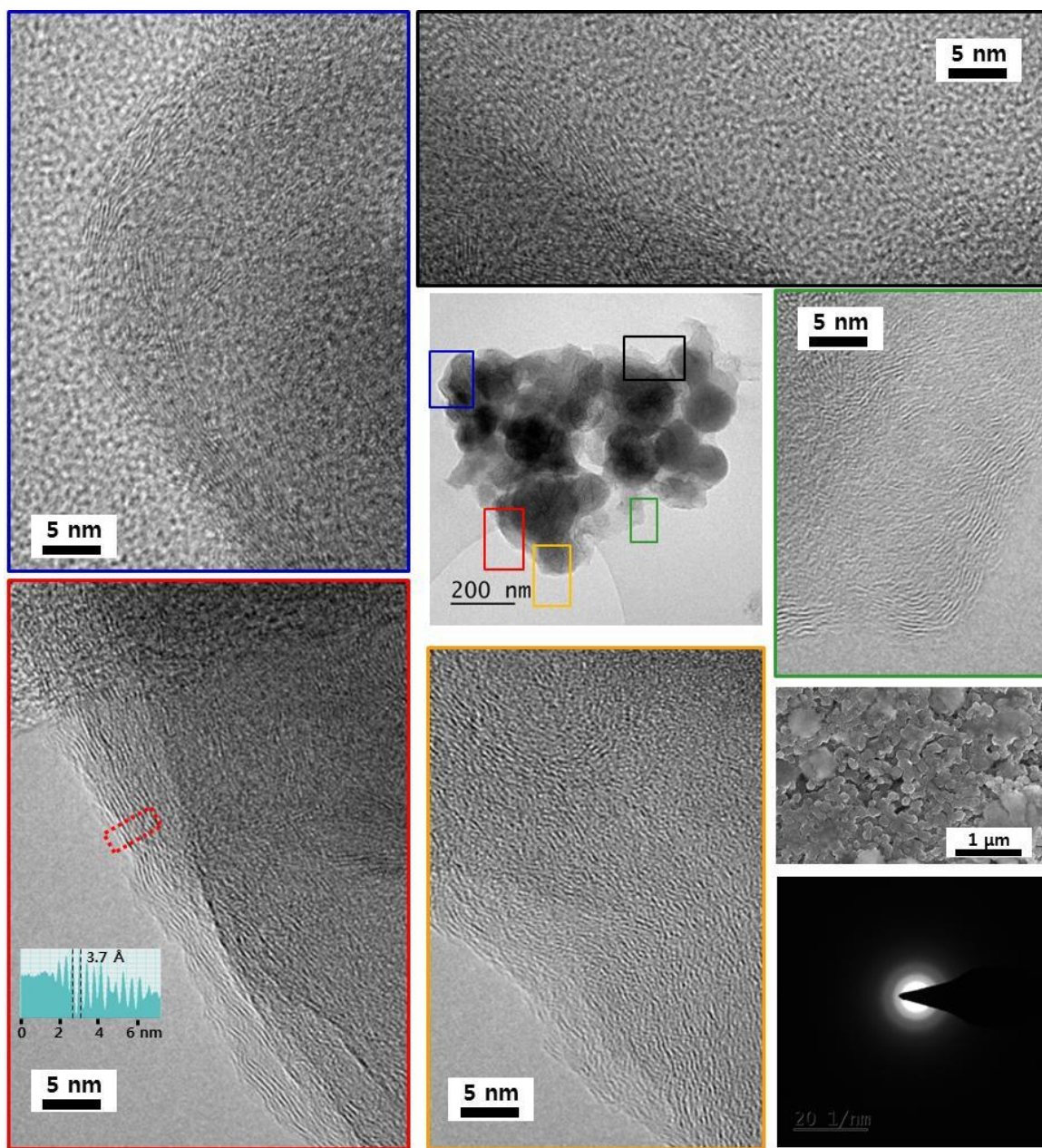
Supplementary Figure 7. Multi-spot TEM analysis of 1wt%-Gr-Si. A lower magnification TEM image of 1wt%-Gr-Si NP ($\text{CO}_2 + \text{CH}_4$ at 1000°C). Higher magnification HR-TEM mages from the color boxes of the center TEM image clearly show graphene layers on Si surface.



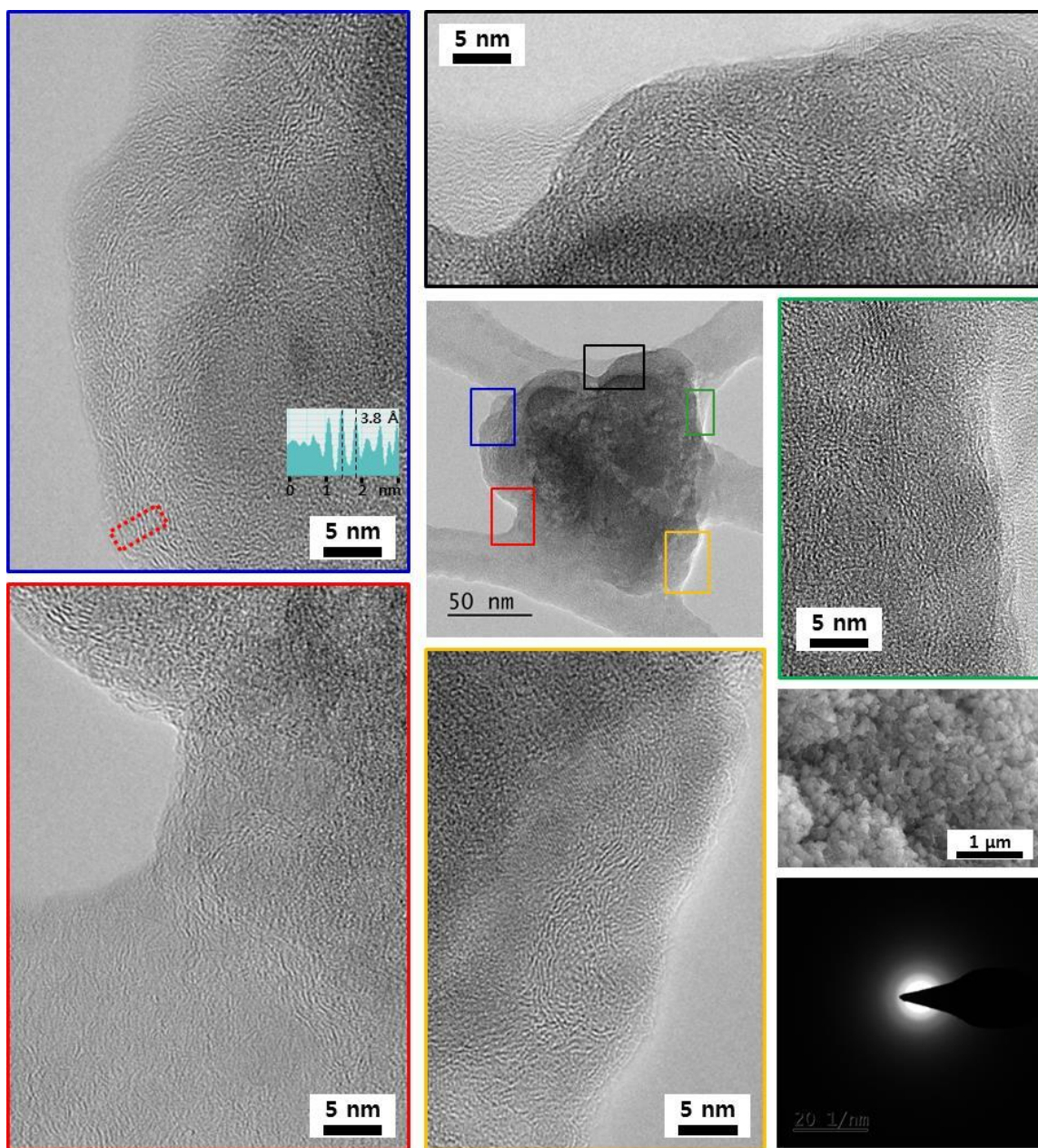
Supplementary Figure 8. Cycling performance. Areal capacity retentions of (a) pristine Si with various Super P contents and (b) 5wt%-Gr-Si with various areal loadings. The binder content was 20 wt%. All the electrodes were cycled at 0.5C for charge and discharge in each cycle. The mass loadings of Si + coated graphene for the different areal capacities are also denoted.



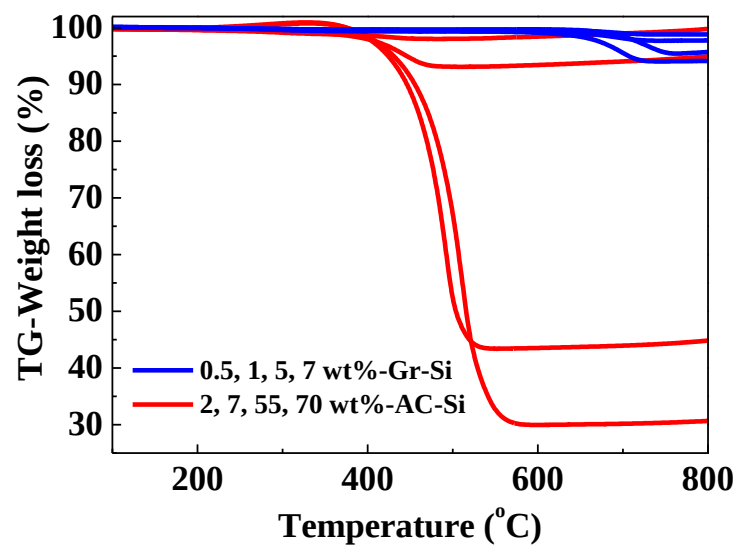
Supplementary Figure 9. *Ex-situ* TEM and SEM analysis of 5wt%-Gr-Si after the 1st lithiation. TEM and SAED images of 5wt%-Gr-Si NPs after the 1st lithiation. Close up HR-TEM images from the color boxes of the center TEM image clearly show graphene layers on Si surface.



Supplementary Figure 10. The same analysis as Supplementary Fig. 9 but after the 1st delithiation.



Supplementary Figure 11. The same analysis as Supplementary Fig. 9 but after the 200th delithiation.



Supplementary Figure 12. Carbon content measurements for Gr-Si and AC-Si. TGA curves of both samples measured at a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ under air.