## **Supporting Information**



Fig. S1 SEM images of Si NPs (a) and Si-CN (b).



Fig. S2 XPS survey (a) and Si 2p XPS (b) spectra of Si NPs, Si-CN, Si@CTF and Si@NPC.



Fig. S3 Discharge-charge curves of Si NPs (a) and NPC (b) electrodes at a current rate of 0.1 A g<sup>-1</sup> for the 1<sup>st</sup>, 2<sup>nd</sup> cycle and 1 A g<sup>-1</sup> for 3<sup>rd</sup>, 10<sup>th</sup>, 100<sup>th</sup> and 200<sup>th</sup> cycle with a cut-off voltage ranging from 0.01 V to 1.2 V (vs. Li/Li<sup>+</sup>). (c) The first discharge curves for Si NPs and Si@NPC electrodes.



Fig. S4 SEM images of Si NPs electrode at fresh state (a) and after 100 cycles at 1 A g<sup>-1</sup> (b); Si@C-CVD electrode at fresh state (c) and after 100 cycles at 1 A g<sup>-1</sup> (d); Si@NPC electrode at fresh state (e) and after 100 cycles at 1 A g<sup>-1</sup> (f).



Fig. S5 TEM (a) and HR-TEM (b) images of Si@C-CVD.



Fig. S6 Nyquist plots for Si NPs, Si@CTF and Si@NPC electrodes before cycling (a) and for Si NPs and Si@NPC electrodes after a fixed capacity (1000 mA h g<sup>-1</sup>) discharging (b).



Fig. S7 TGA curve of Si@C-CVD in air atmosphere.