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Supporting information

Figure S1. The photos of four kinds of Si-material.



Fig. S2. (a) The comparison figure N2 adsorption / desorption isotherms on both surface of silicon nanoparticles and assembly microsphere. (b) Pore size distribution plots of SiNPs and CSs by Barrett–Joyner–Halenda (BJH) method.



Figure S3. X-ray diffraction pattern (XRD) for SiNPs, CNTs and CNTs-Si composite microspheres (CSs).



Figure S4. Active material of SiNPs or SiMPs contain 30 wt% CNTs and CNTs:SiNPs=3:7 in CSs.



Figure S5. Typical SEM images of (a) alloying state of CSs and (b) alloying state of PSs after 100 cycles.



The peculiar structure for CSs that Si nanoparticles are adsorbed on the surface of the carbon nanotubes and assembled to microspheres demonstrate the electrochemical performance of the long-term stability during repeatedly charge-discharge.





Figure S7. Apparent Diffusion coefficient of lithium ion in microspheres. (a) τ vs E profile for a single GITT titration.



A constant current density (I_0) duration for 20 min are applied to the Si-electrode for a limited time period (t_0), and Li-ions insert into the electrode grains and form a concentration gradient from surface to inner of particle. In turn, an open-circuit voltage (E_0) were detected, and a diffusion equilibration of Li-ions during E_0 periods causes a change of voltage. This varies be considered the change of Li-ion concentration on surface and inner of particle, and the diffusion coefficient (D_{Li}^+) within the active material can be calculated [1]

$$D_{Li^+} = \frac{4}{\pi\tau} \left(\frac{m_B V_m}{M_B A}\right)^2 \left(\frac{\Delta E_S}{\Delta E_\tau}\right)^2 \qquad \qquad (\tau \ll \frac{L^2}{D_{Li^+}})$$

 m_B (g), M_B (g mol⁻¹), V_m (cm³ mol⁻¹), A (cm²), and L(cm) are the mass of active material, molecular weight, molar volume, surface area and thickness of electrode, respectively. ΔEs and $\Delta E\tau$ are steady-state (equilibrium) voltage and the total change of the cell voltage E during the current pulse.

Figure S8. EIS curves for PSs electrodes (a) and equivalent circuit (b).



The EIS curves contain the semicircle in high-frequency and a following line in lowfrequency. The intercept of super-high frequency at real part (*Z*') corresponds to the equivalent series resistance (Resr), which is mainly induced from the Ohmic resistance of the electrodes. The diameter of the semicircle in high-frequency represents the charge-transfer resistance (Rct) containing the Faradic reactions and the double-layer capacitance (Cdl) between electrode and electrolyte. A slop line in the low-frequency range is called the Warburg resistance (Zw) and is relative to the ionic transport and diffusion resistance.

Reference

[1] M. J. Yacaman, M. M. Yoshida, L. Rendon, Appl. Phys. Lett. 1993, 62, 202-204.