

Supplementary Information

A novel material of Co-Li₂O@Si core-shell nanowire array composite as a high-performance lithium-ion battery anode

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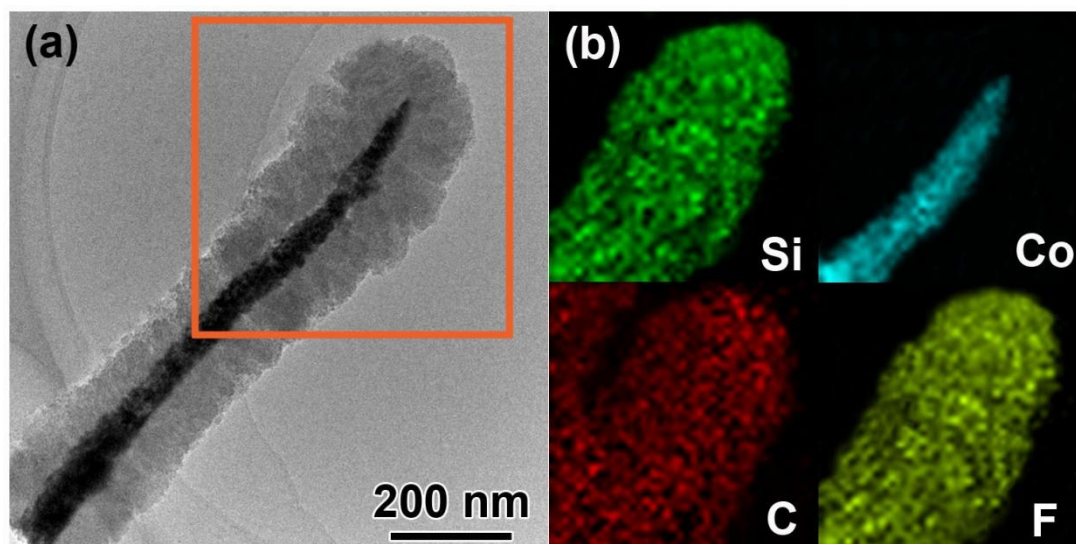


Fig.S1 (a) TEM image of Co-Li₂O@Si core-shell nanowire arrays after 200 cycles at a current density of 840 mA g⁻¹; (b) corresponding EDX spectrum of (a).

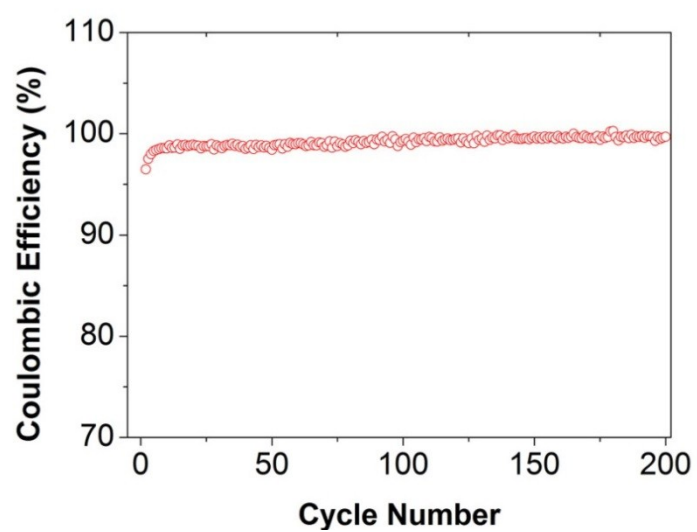


Fig. S2 Coulombic efficiency *versus* cycle numbers for the CoO-Si electrode at a current density of 840 mA g⁻¹

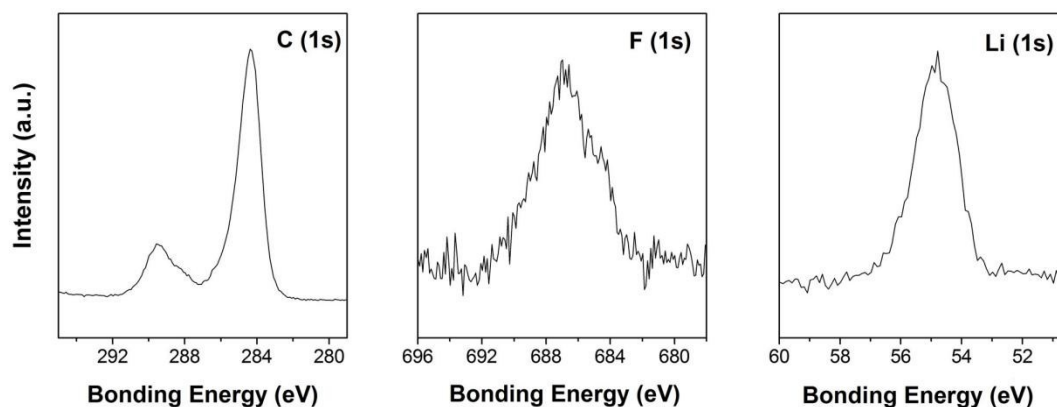


Fig.S3 XPS spectra of Co-Li₂O@Si core-shell nanowire electrode at 0.3 C after 200 cycles.

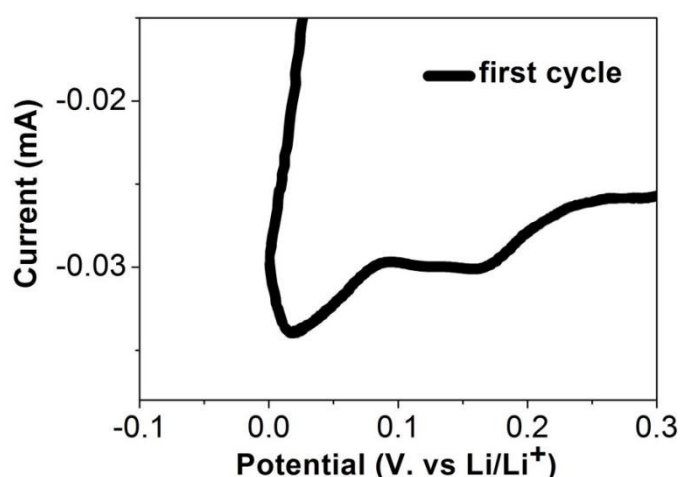


Fig.S4 One magnified segment of the CV curves of CoO@Si core-shell nanowire array electrodes for the first cycle.

Fig. S1a shows TEM examination of Co-Li₂O@Si core-shell nanowire electrode after long cycles. As observed, it did not show thick SEI layers, but did show that the core-shell nanowire structure was well preserved (Fig. S1a). We attribute this to the unique Co-Li₂O@Si core-shell architecture, which consists of the nanocolumnar Si shell that remains intact after long cycling (Fig. 9). The void space between the nanocolumnar Si acts as galleries for fast Li diffusion in electrolyte and significantly shortened the Li path length in solid Si. In addition, as observed in Fig. S1b, the corresponding elemental mappings indicate the homogeneous distribution of F and C

signals over the delithiated sample. The F and C signals may come from the SEI layers consisting of LiF, Li_2CO_3 , and so forth (Pallavi Verma, et al., *Electrochimica Acta*, 2010, 55, 6332). An expected thin SEI veil forms over the individual Si nanowires, providing a flexible sheath that prevents the Si nanowires from coalescing or breaking off during lithiation/delithiation-induced expansion/contraction. These results demonstrate that the core-shell nanowire structure and the SEI layer can be effectively restrained upon cycling, which plays an important role in the enhanced Li-storage performance.

Fig. S2 shows the Coulombic efficiency (CE) *versus* cycle numbers at a current density of 840 mA g^{-1} for CoO@Si electrode. We notice that the CE reached 95% at the second cycle while the others stay steadily above 98% thereafter. The high CE indicates that the SEI layers and the anode material keep stable during cycling. This can be ascribed to the fact that CoO nanowires maintain a direct electrical connection with the substrate, thereby facilitating electron collection and transport. The CE results further confirm that the SEI layer and the core-shell structure can be effectively restrained upon cycling.

In order to investigate the composition of the SEI layer on the Si thin electrode after long cycling, the Si electrode was analyzed by XPS. The electrodes were washed with DMC (dimethyl carbonate) to remove the residual electrolyte components such as organic solvents and lithium salt and then vacuum-dried at room temperature to evaporate the DMC. Fig.S3 shows the XPS spectra for the Co-Li₂O@Si electrode after 200 cycles. The C 1s peak in Fig. S3 shows a prominent peak centered at 285 eV and a small peak at $\sim 289 \text{ eV}$. The latter is assigned to the C atoms bonded with three oxygen atoms, such as in the cases of lithium carbonate Li_2CO_3 and lithium alkyl carbonates ROCO_2Li . These compounds have already been known in the SEI layers of different electrodes. The Li 1s spectrum mainly shows a peak at $\sim 55.8 \text{ eV}$ that may be attributed to the component of LiF. The F 1s spectrum in Fig. S3 displays a peak at $\sim 687 \text{ eV}$, consistent with LiF. All the peaks are calibrated by C 1s of hydrocarbons at 285 eV.