## **Supporting Information**

## **Supplementary figures**



Supplementary Figure S1. Wafer scale monolayer PS nanosphere templates and Si NR arrays can be successfully fabricated using the spin-coating method: (a) The SEM images of the as-fabricated PS template by assembling the 300-nm-diameter PS nanospheres and the inset-photograph of the self-assembled PS nanospheres monolayer on a 4 inch silicon wafer;
(b) The SEM images of the as-fabricated Si NR arrays using the NSL combined ICP etching method and the inset-photograph of the fabricated Si NR arrays on the 4 inch silicon substrate by employing the PS template of (a);



**Supplementary Figure S2**. The average diameters of PS nanospheres were manipulated linearly by O<sub>2</sub> plasma etching for 0, 30 and 60 s, respectively.



Supplementary Figure S3. The capacity retention of the Si/SnO<sub>2</sub> NR composite electrode at a current density of 500  $\mu$ A cm<sup>-2</sup> after the CV measurement of six cycles.

The CV measurement of the first cycles within the voltage window between 0.01 and 2.0 V vs. Li/Li<sup>+</sup> can act as the activation process. It is clear that the discharge capacity (Li-ion insertion) during the first 20 cycles decreases rapidly, and then reaches to a relatively stable state. After 200 cycles, the discharge capacity still can be maintained at about 0.2 mAh cm<sup>-2</sup>.



**Supplementary Figure S4.** (a) SEM images of Si/SnO<sub>2</sub> NR composite electrode in a large area after 200 cycles at a current density of 500  $\mu$ A cm<sup>-2</sup> within the voltage window from 0.1 to 2.0 V *vs.* Li/Li<sup>+</sup> and its high magnification morphology with the volume expansion of the active material as in the inset; the corresponding TEM images of (b) the Si/SnO<sub>2</sub> NR composite arrays remaining the bottle-like structures and (c) minor peeling-off phenomena on the Si/SnO<sub>2</sub> NR surface induced by the cycling processes.