## **Supplementary Information**

## **Highly Stable Si-based multicomponent anodes for practical use in lithium-ion batteries**

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**Figure S1.** Characterization of  $Si-SiO-SiO<sub>2</sub>$  three-component prepared by thermal annealing of SiO particles in the presence of NaOH. Sodium silicate was formed on the surface of Si-based particles. Sodium peak was detected by EDAX profile. Sodium silicate was not detected by XRD due to a limited amount.



Figure S2. XRD patterns of bare SiO and Si-SiO-SiO<sub>2</sub> three-components prepared by three different annealing times at a fixed temperature of 800  $^{\circ}$ C. As the annealing time increased, the peak intensities of cristobalite and silicon increased with an increasing annealing time.



**Figure S3.** Crystallization of amorphous silica in the presence of NaOH (weight ratio of SiO to NaOH = 20:1) at 800 °C for 10 min. A great part of amorphous silica was converted into crystialline silica (cristobalite phase).



**Figure S4.** Characterization of Si-SiO-SiO<sub>2</sub> multicomponents. (a) TEM image showing cristobalite layers in the outer shell of samples annealed at 800  $^{\circ}$ C for 2 hr. Box area in the figure indicates the crystalline silica, cristobalite. (b) Selected area diffraction pattern obtained from the cristobalite layer.



**Figure S5.** Time-of-flight secondary ion mass spectroscopic mapping of as-prepared Sibased multi-component (a, b) and depth profiled samples (c, d). The Si-based multicomponent was prepared at 800  $^{\circ}$ C for 10 min in the presence of NaOH. The asprepared Si-based multi-component showed that the  $SiO<sub>2</sub>$  phases were clearly detected on the top surface. After depth profiling  $(-10 \text{ nm})$ , the intensity of Si phases were much stronger than those of  $SiO<sub>2</sub>$  phases. It indicated that most  $SiO<sub>2</sub>$  layer was etched out in the Si-based multi-component.



**Figure S6.** Bright-field TEM image showing nanocrystalline silicon dispersed in a SiO matrix. The dotted circle shows the crystalline silicon.



**Figure S7.** Cycling performance of c-Si-multi-20-1 electrode at 0.1C (1-120 cycles) and 0.2C (121-200 cycles) in the range of 0.005-2.0V.



**Figure S8.** TEM images of c-Si-multi-20-1 and c-SiO electrodes after 100 cycles at a rate of 0.2C. The c-Si-multi sample showed that Si nanoparticles having an average diameter of 15 nm were uniformly dispersed in the SiOx matrix. However, a serious arregation of Si phase was observed in the c-SiO.



**Figure S9.** Electrochemical performances of SiO thermally annealed at 1000 °C for 3 hr without NaOH. a) Voltage profiles (First cycle) of disproportionate SiO (d-SiO) and the carbon-coated d-SiO obtained at 0.1 C rate in the range of 0.005 and 2.0 V. b) Cycle retention of the d-SiO and the carbon-coated d-SiO.