Electronic Supplementary Information

Construction of hybrid bowl-like structures by anchoring NiO nanosheets on flat carbon hollow particles with enhanced lithium storage properties

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Experimental details

Material synthesis

All reagents were analytical grade and used without further purification.

Bowl-like sulfonated polystyrene hollow particles (SPS): After drying the emulsion (EPRUI Nanoparticles & Microspheres Co. Ltd.) at room temperature, the bowl-like hollow polystyrene particles were obtained. Sulfonated polystyrene was prepared according to a previously reported method. In a typical synthesis, bowl-like hollow polystyrene particles (2 g) were added to concentrated sulfuric acid (polystyrene : H_2SO_4 = 1 : 30, w/w) and the mixture was under sonication for 10 min to ensure good dispersion. After being stirred for 0.5 h at 40 ℃, the pinkish precipitate was collected by centrifugation and washed thoroughly with ethanol.

Ni-precursor@SPS: 375 mg of $Ni(NO_3)_2 \cdot 6H_2O$ and 175 mg of hexamethylenetetramine were dissolved into 200 mL of 0.7 mM trisodium citrate solution. Then 50 mg of SPS was dispersed into the above solution by sonication for 30 minutes. The reaction mixture was then transferred into a 500 mL round bottom flask. After stirring for 6 h at 90 ℃, the flask was left to cool down to room temperature. The green precipitate was collected by centrifugation, washed thoroughly with ethanol, and dried at 60 ℃ overnight.

Bowl-like NiO NSs@C particles, spherical NiO NSs@C hollow particles and NiO NSs particles: the as-prepared Ni-precursor@SPS composite was subjected to calcination at 500 ℃ for 3 h in nitrogen, and then the bowl-like NiO NSs@C particles were obtained. Spherical NiO NSs@C hollow particles and NiO NSs particles were prepared via a similar procedure with bowl-like NiO NSs@C particles in the presence of conventional spherical polystyrene template and without template, respectively.

Materials characterization

The morphology and microstructure of the products were characterized by field-emission scanning electron microscopy (FESEM; HITACHI, su-8010), and transmission electron microscopy (TEM; JEOL JEM-2100) with selected-area electron diffraction pattern (SAED) function. The composition and crystal structure were characterized by X-ray diffraction measurement (XRD; SHIMADZU, Lab X XRD-6000). Thermogravimetric analysis (Perkin–Elmer TGA 7) was carried out under a flow of air with a temperature ramp of 10 ^{o}C min^{-1} from room temperature to 600 ^{o}C.

Electrochemical characterization

Electrochemical measurements were performed using CR2025-type coin cells assembled in an argon-filled glove box (China, Dellix, $[O_2]<1$ ppm, $[H_2O]<1$ ppm). Pure lithium foil was used as the counter electrode. The working electrodes were composed of the active material, conductive material (carbon black, C-NERGYTM Super C65), and binder (poly-vinyldifluoride, PVDF) in a weight ratio of active material/C65/PVDF=70:20:10 and pasted on Cu foil. Pure lithium foil was used as the counter electrode. Microporous membrane (PP/PE/PP) from Celgard was used as the separator. The electrolyte used was a mixture of ethylene carbonate and dimethyl carbonate (EC+DMC) (1:1 in volume) containing 1.0 M $LiPF_6$.

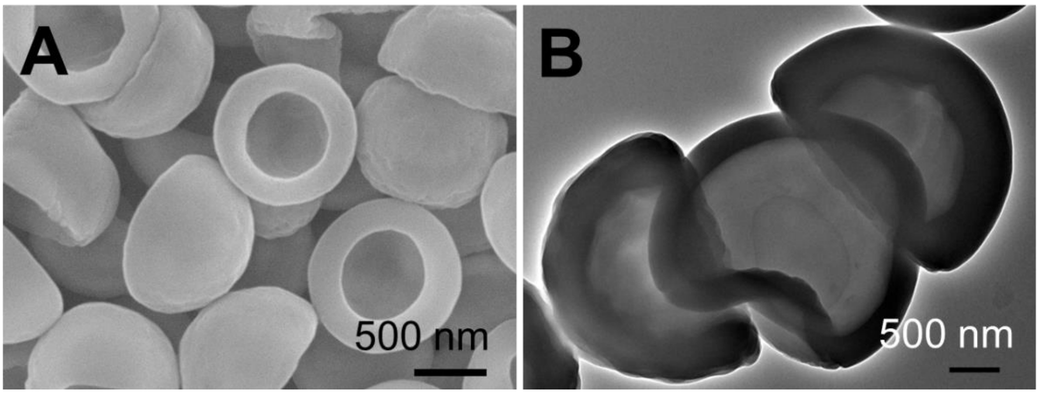

Fig. S1 A) FESEM and B) TEM images of bowl-like sulfonated polystyrene particles.

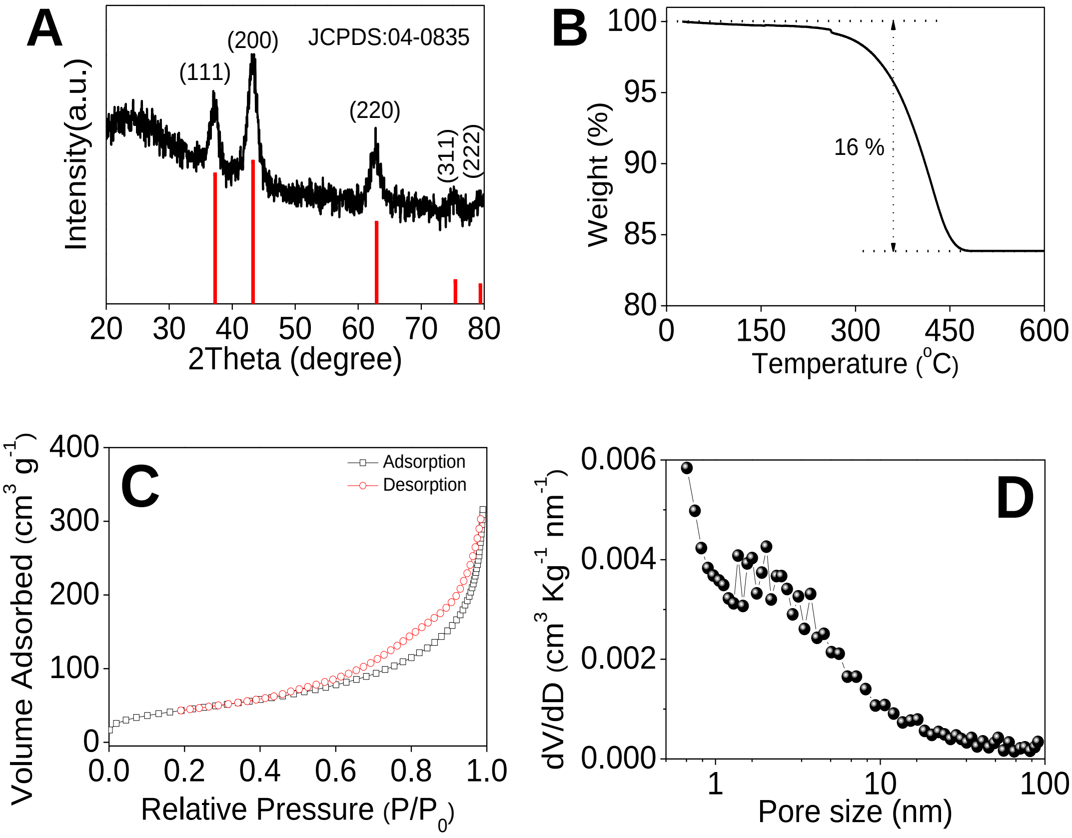

Fig. S2 A) XRD pattern, B) TGA analysis, C) N_2 adsorption–desorption isotherms of the bowl-like NiO NSs@C particles. D) The pore-size distribution calculated from the adsorption branch.

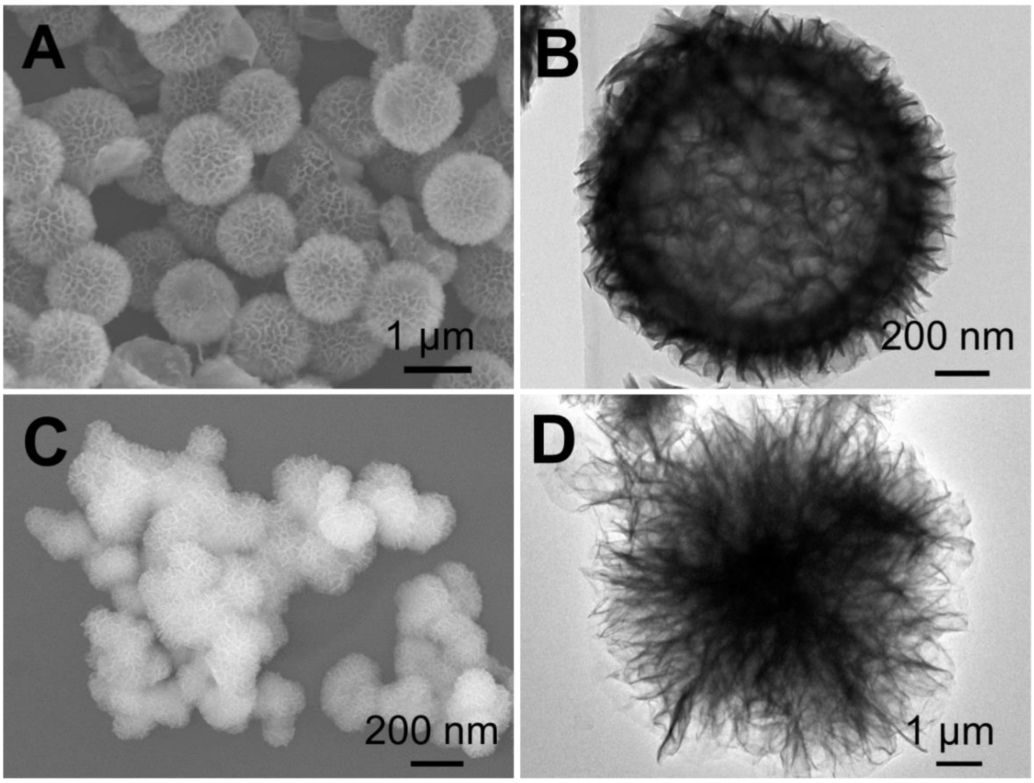

Fig. S3 FESEM and TEM images of: A, B) spherical NiO NSs@C hollow particles; C, D) NiO nanosheets hierarchical particles.

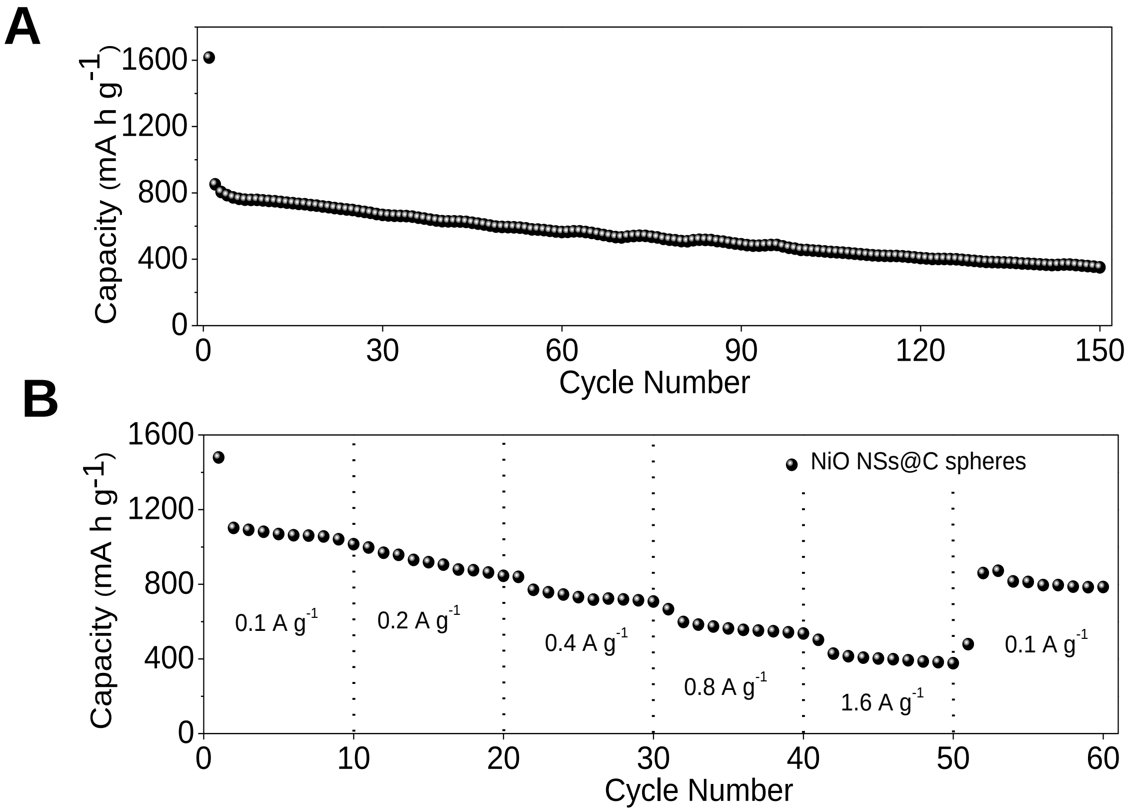

Fig. S4 Electrochemical performance of spherical NiO NSs@C hollow particles: A) cycling performance at a current density of 0.4 A g^{-1}; B) rate capability at different current densities in the voltage window of 0.01 - 3.0 V.

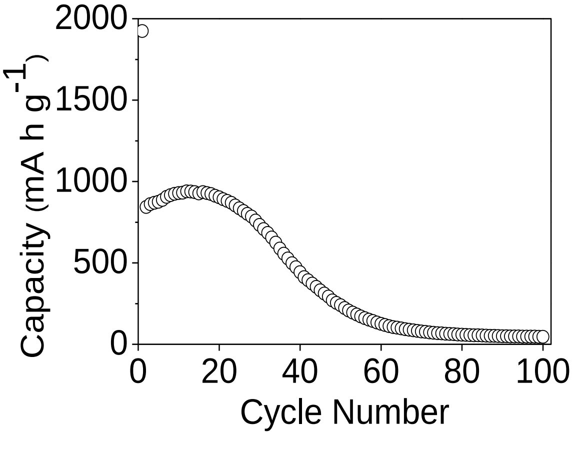

Fig. S5 Cycling performance of NiO NSs particles at a current density of 0.4 A g^{-1}.

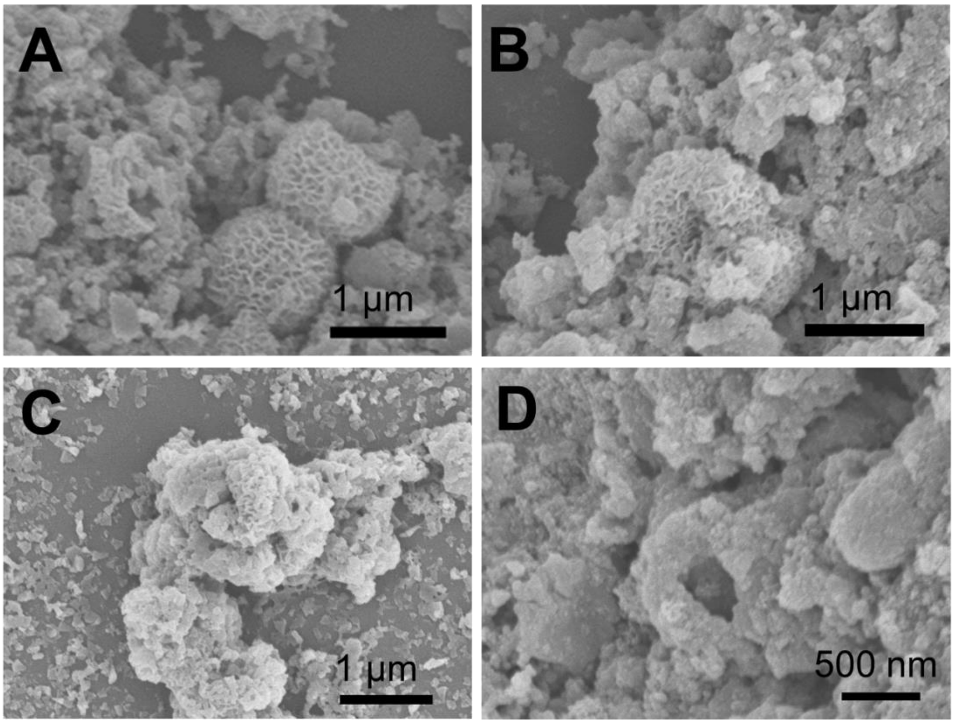

Fig. S6 FESEM images showing the morphology of the bowl-like NiO NSs@C particles after A) 1, B) 5, C) 15 and D) 28 charge-discharge cycles at a current density of 0.4 A g^{-1} between 0.005 V and 3.0 V. As expected, the overall structure of the electrode is less defined due to complex composition of the electrode and possible physical damage during the handling of the electrodes after cycling.

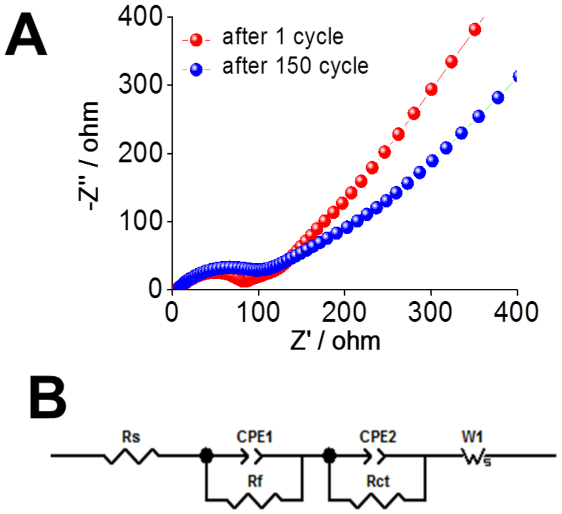

Fig. S7 A) Nyquist plots of the cell after 1 and 150 cycles obtained by applying a sine wave with amplitude of 5.0 mV over the frequency range from 100 kHz to 0.01 Hz; B) equivalent circuit model of the studied system. CPE represents the constant phase element.

R_s represents the internal resistance of the cell, R_f is associated with the resistance of the SEI film, R_{ct} is associated with the charge-transfer resistance and constant phase. W_s is associated with the Warburg impedance corresponding to the Li$^+$ diffusion process. As shown in Fig. S7A, the high-frequency semicircle corresponds to the resistance R_f of the SEI film, and the semicircle in the medium-frequency region is assigned to the charge-transfer resistance R_{ct} of the electrode/electrolyte interface. The inclined line corresponds to the Li$^+$ diffusion process within the bulk of the electrode material. The kinetic differences of the bowl-like NiO NSs@C electrode after 1 and 150 cycles were further investigated by modeling AC impedance spectra based on the modified equivalent circuit. The R_f increases from 1.87 Ω initially to 5.26 Ω after 150 cycles due to the formation of SEI film. Note that the charge-transfer resistance R_{ct} of electrode after 150 cycles is 91.56 Ω which is slightly higher than that after the initial cycle (81.88 Ω).

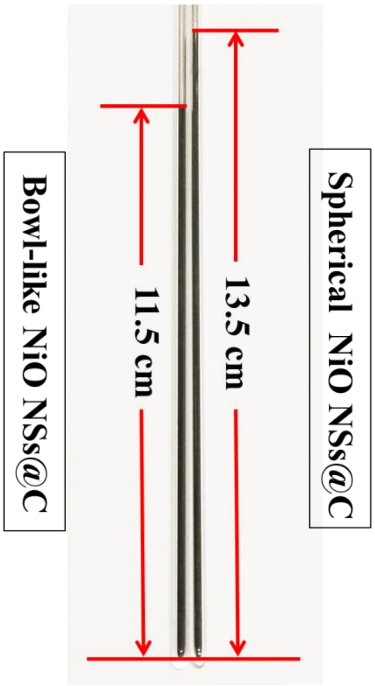

Fig. S8 A digital photo showing 150 mg of bowl-like NiO NSs@C particles and spherical NiO NSs@C composites tapped in quartz tubes with inner diameter of ca. 3 mm. The increase in tapped density of the bowl-like particles is below intuitive expectation, which could be ascribed to the imperfect alignment of the bowl-like particles.