Supplementary information

Hierarchical nanostructured nickel cobalt oxides microspheres composed of mesoporous nanothorn array and their superior rate capability as anode materials for lithium ion batteries

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1. Experimental details

1.1. Raw materials

In this work, Urea (Purity≥99%, Xilong Chemical Co., Ltd.), $NiCl_2·6H_2O$ (Purity≥98%, Xilong Chemical Co., Ltd.), $CoCl_2·6H_2O$ (Purity≥99%, Sinopharm Chemical Reagent Co.,Ltd) and distilled water were used as raw materials without further purification to prepare the precursor and final products nickel cobalt oxides (NCO).

1.2. Synthesis of $Ni_{1.5}Co_{1.5}O_4$ thorn spheres

In a typical preparation process, stoichiometric urea, $NiCl_2·6H_2O$, $CoCl_2·6H_2O$ in a molar ratio of 2/1/1 were firstly dissolved into 60 ml distilled water under vigorous magnetic stirring, respectively. Subsequently, the obtained clear mixed solution was transferred into a 100 ml Teflon container, and then sealed into a stainless steel autoclave. Thereafter, the sealed autoclave was put into a blowing dry box which had been pre-heated to 120 °C. To

obtain the designed nanostructure, the self-assembling hydrothermal reaction was continuously carried out at 120 °C for 16h. After being washed with distilled water for 3 times, the obtained products were dried at 60 °C for 10h and collected as precursor for preparing the final product NCO. Finally, the final product NCOs were obtained by annealing the precursor obtained above at a relatively low temperature 400, 500 and 600 °C for 2h under air condition. The obtained NCOs were marked as NCO-400, NCO-500 and NCO-600, respectively. The temperature were determined according to the differential thermal analysis results of precursor.

1.3. Characterization

The morphology of as-prepared precursor and final products are characterized by using field emission scanning electron microscopy (FE-SEM, Hitachi S-4800) at an acceleration voltage of 15 kV and field emission transmission electron microscope (FE-TEM, JEOL 2010F) at an accelerating voltage of 200 kV. Nitrogen adsorption/desorption isotherms were obtained at 77 K using an automated adsorption apparatus (Micromerit-ics ASAP 2020). The surface area was calculated based on the Brunauer–Emmett–Teller (BET) equation. The X-ray diffraction patterns of as-prepared precursor and final products are measured on an X-ray diffractometer (RIGAKU, RINT-ULTIMA III) using Cu Kα radiation (λ= 1.54051Å). The diffraction patterns were recorded in the 2θ range of 10-70 ° with a step size of 0.01 °. The thermal properties of the as-prepared precursor was measured by using the PERKIN—ELMER Diamond TG/DTA differential thermal analyser.

In order to investigate the electrochemical performance of as-prepared NCO thorn spheres, the composite electrodes of NCOs were prepared by coating the uniform slurry of NCOs mixed with acetylene black (AB) and Polyvinylidenefluoride (PVDF) (NCO/C/PVDF=75/15/10). The electrode was then pressed and punched out into 10 mm disks in diameter. Two-electrode lithium ion batteries were assembled in an ultrapure Ar-gas filled glove box to study the lithium ion storage performance of NCOs in the electrolyte of 1 mol L^{-1} $LiPF_6$ in ethylene carbonate (EC) + dimethyl carbonate (DMC) + Ethyl methyl carbonate (EMC). Lithium discs were used as counter and reference electrodes. Cyclic voltammetry (CV) and galvanostatic charge and discharge measurements were carried out in

the electrolytic window range of 0.02 to 3 V vs Li/Li^+ at the current range of 0.18 - 4.5 A g^{-1}, respectively.

2. Supplementary results

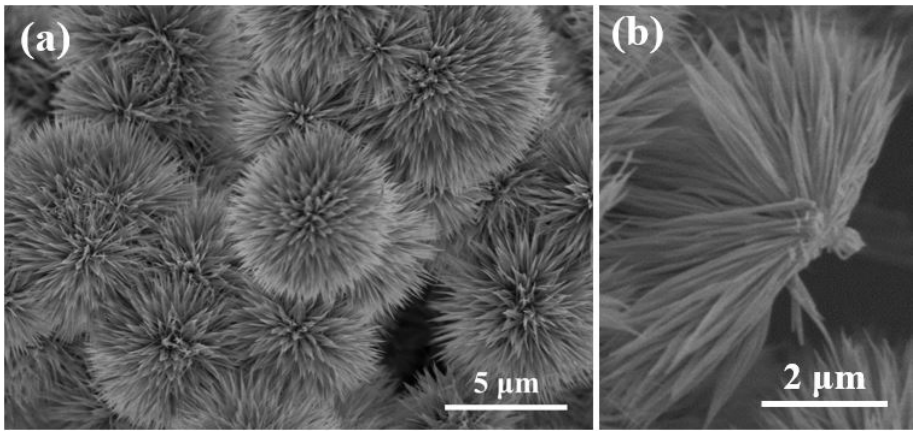

Fig. S1. The low magnification (a) and high magnification (b) SEM image of as-prepared precursors $NiCo(OH)_2CO_3$

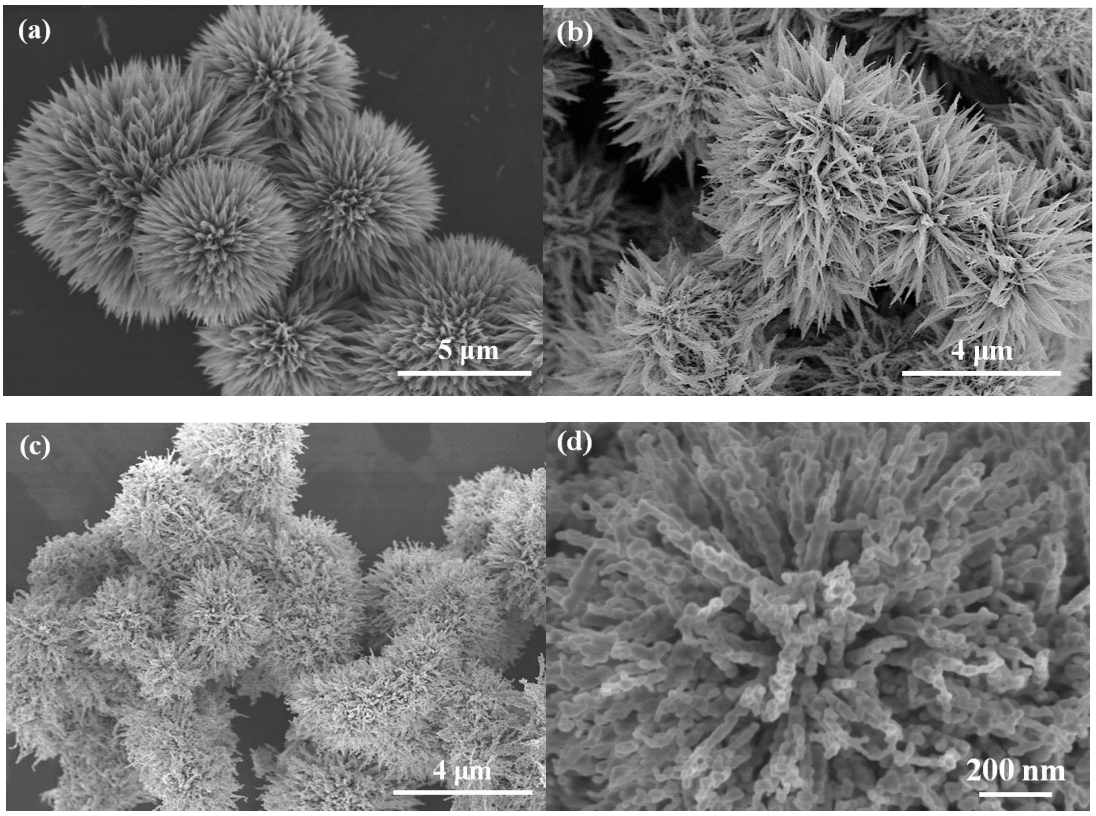

Fig. S2. The low magnification SEM image of (a) NCO-400, (b)NCO-500 and (c, d) NCO-600.

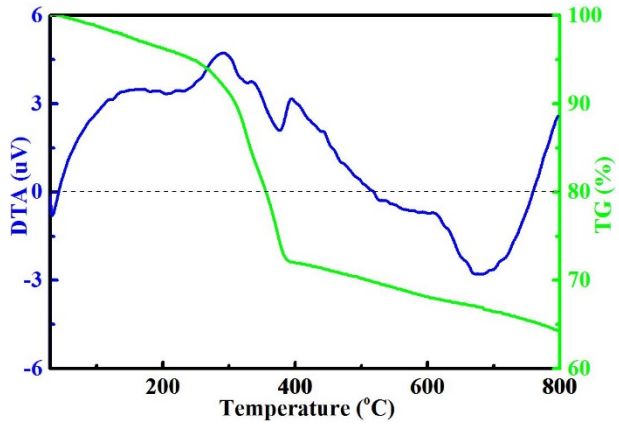

Fig. S3. The TG/DTA analysis results of the as-prepared $NiCo(OH)_2CO_3$ precursor

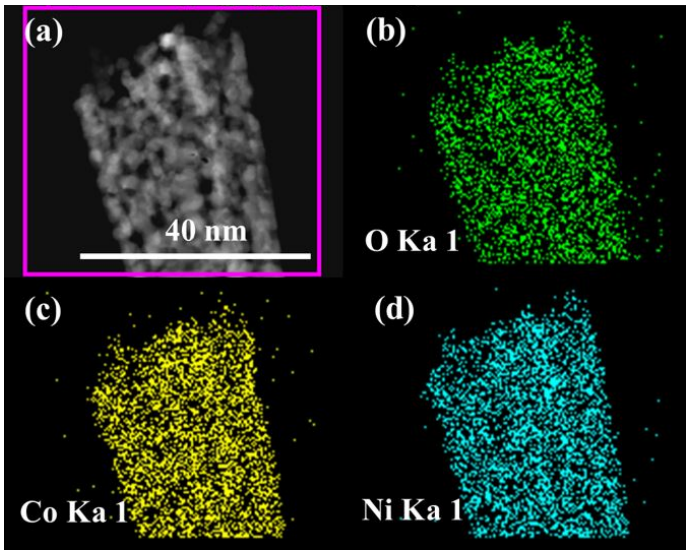

Fig. S4. FE-TEM image (a) and corresponding EDX mapping for O(b), Co(c) and Ni(d) of NCO-400, respectively.

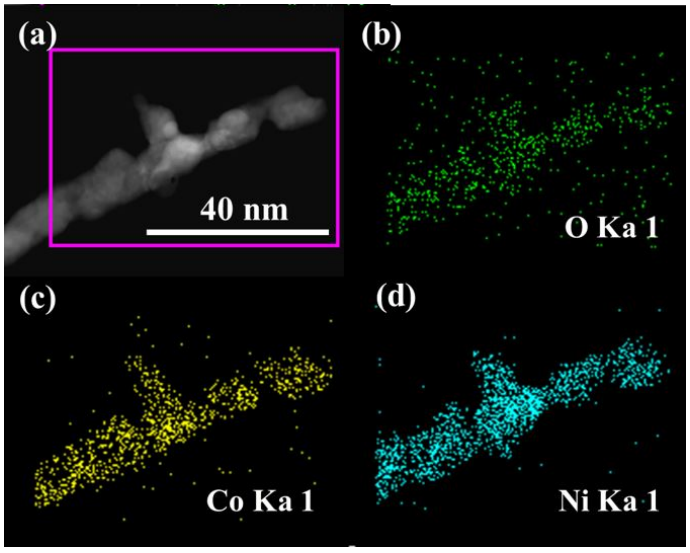

Fig. S5. FE-TEM image (a) and corresponding EDX mapping for O(b), Co(c) and Ni(d) of NCO-500, respectively.