

Electronic Supplementary Information

Confined formation of monoclinic $\text{Na}_4\text{Ti}_5\text{O}_{12}$ nanoparticle embedded
into porous CNTs: towards enhanced electrochemical performances
for sodium ion batteries

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Experimental Section

Materials: Divinyl benzene (80 %) (DVB) and boron trifluoride diethyl etherate complex were purchased from Aladdin Reagent Company and 4-vinylbenzylchlorid (90 %) (VBC) was purchased from J&K Chemical Reagent Company. All other reagents were commercially available with AR grade and used without further purification. Poly (divinylbenzene-co-4-vinylbenzylchlorid) nanotubes (PNTs) and sulfonated polymer nanotubes (SPNTs) were prepared according to our previously reported methods.^{1,2}

Synthesis of Hybrid Porous CNTs with Embedded M-Na₄Ti₅O₁₂ Nanoparticles: Firstly, 70 mg SPNTs powder was dispersed in 5 mL ethanol with ultrasonication for 30 min. Secondly, 5 g TBT was added and stirred for 12 h at room temperature to allow a saturated adsorption of the gel into walls of the SPNTs. After centrifugation, the residue was carefully collected and wiped with a piece of tissue paper to remove the excess liquid. The obtained powder was dried in air at 80°C for 12 h, which was denoted as ST. Then, 200 mg ST and 90 mg Na₂CO₃ powder were mixed and ground in an agate mortar for 15 min at room temperature. The mixture was calcined at 850°C for 6 h in N₂ at a heating rate of 5°C min⁻¹, resulting in M-Na₄Ti₅O₁₂ nanoparticles embedded in porous CNTs. The obtained hybrid is denoted as MNTO/C.

Materials Characterization: Morphologies and structure features of the samples were studied by using field emission scanning electron microscope (FESEM Hitachi S-4800) and high resolution transmission electron microscope (HRTEM JEOL JEM-2010F). Phase compositions of the samples were characterized by using X-ray diffraction (XRD, Bruker

D8 advance with Cu Ka radiation). Thermogravimetric analysis (TGA) was carried out by using a Netzsch STA 449C at a heating rate of $10^{\circ}\text{C min}^{-1}$ from 30 to 800°C in air. Nitrogen adsorption-desorption isotherms were recorded by using an Autosorb-iQ Pressure Sorption Analyzer (Quantachrome Instruments U. S.) at 77 K. Specific surface areas of the samples were calculated by using the Brunauer-Emmett-Teller (BET) method, while pore size distributions were calculated by using the Density Functional Theory (DFT) method.

Electrochemical Characterization: 2032 coin cells were adopted to measure electrochemical performances of the sample, whereas Na metal was used as the counter and reference electrodes. 70 wt% active materials, 20 wt% carbon black and 10 wt% poly (vinylidene fluoride) binder were dispersed in N-methyl-2-pyrrolidone to form slurries, which were casted on Cu foil and dried at 110°C overnight in vacuum. All cells were assembled in an argon-filled glove box, with glass fiber as the separator and NaClO_4 (1 M) in ethylene carbonate/dimethyl carbonate (1:1 vol) as the electrolyte. Cyclic voltammograms (CVs) were collected by using an electrochemical workstation (CHI660D, Chenhua, China) at a scan rate of 0.1 mV s^{-1} . Galvanostatic charge-discharge tests were carried out by using a Land (CT2001A China) between 0.01 and 3.00 V (versus Na^+/Na).

References

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2. W. Ni, F. X. Liang, J. G. Liu, X. Z. Qu, C. L. Zhang, G. L. Li, Q. Wang and Z. Z. Yang, *Chem. Commun.*, 2011, **47**, 4727-4729.