Supporting Information

Open Holey Structure Enhanced Superior Rate Capability in $NaTi_2(PO_4)_3$/C Nanocomposite for Ultralong-Life Sodium-Ion Storage

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EXPERIMENTAL SECTION

Synthesis of the NTP/C Nanocomposites. First, the anhydrous sodium acetate (5 mmol, CH_3COONa) and tetrabutyl titanate (4 mmol, $C_{16}H_{36}O_4Ti$) were slowly added in the ethanol (40 mL, C_2H_5OH). After obtaining a clear and homogeneous solution, phosphoric acid (5ml, H_3PO_4) was added to the above solution under continuous stirring. Then the obtained homogenous milky solution was moved into a sealed Teflon reactor and heated at 210 °C for 24 h. When the reactor cooled to room temperature, the white product was washed with water and ethanol for three times, respectively. After that, it was dried in a blast oven for 1 h at 80 °C to obtain the NTP species. Subsequently, the NTP and glucose were mixed thoroughly by grinding. Finally, the as-prepared precursor was annealed at 800 °C for 24 h in Ar atmosphere to generate the NTP/C-24h nanocomposite. In order to study the effect of solvothermal time on the battery performances, two counterparts of NTP/C-6h and NTP/C-48h nanocomposites were prepared through the same procedure except the solvothermal time of 6 and 48 h, respectively.

Material Characterizations. The crystal structures of the NTP/C nanocomposites were characterized by X-ray diffraction (XRD, Bruker D8 Advance diffractometer) with Cu Kα radiation (λ = 1.5405 Å). The morphological and microstructural characterizations of the NTP/C nanocomposites were visualized by scaning electron microscopy (SEM, ZEISS Supra 55) and transmission electron microscopy (TEM, FEI TecnaiG2 F30). The thermal stability of the NTP/C nanocomposites was evaluated by thermogravimetric analysis (TGA, Mettler-Toledo TGA/DSC-1 system). Brunauer-Emmett-Teller (BET) measurements of the NTP/C nanocomposites were performed by Micromeritics ASAP 2020.

Electrochemical Performances of the NTP/C Nanocomposites. All the electrochemical properties of the NTP/C nanocomposites were performed at room temperature using a half-cell configuration. The NTP/C electrodes were prepared by mixing the NTP/C nanocomposites, conductive materials (acetylene black and ketjenblack, 1 : 1 in weight), and binder (polytetrafluoroethylene) onto copper foils in a weight ratio of 7 : 2 : 1. In the half cells, sodium foil was used as the counter electrode, $NaClO_4$ solution (1 mol L^{-1}) in ethylene carbonate (EC) and dimethyl carbonate (DMC) (1 : 1 in volume) was used as the electrolyte, and the glass fiber was used as the separator. The electrochemical tests were performed at various rates (1 C corresponds to 133 mA g^{-1}) between 1.5 and 3.0 V on a NEWARE battery test system. The delivered capacities of the three NTP/C nanocomposites are all calculated based on the mass of the whole NTP/C instead of pure NTP. Cyclic voltammetry (CV) measurements were conducted at various scan rates on the AMETEK Solartron analytical 1407E. Electrochemical impedance spectroscopy (EIS) measurements were performed within the frequency range of 0.01 to 10^5 Hz on a CHI660D electrochemical workstation (Chenhua Instrument Company, Shanghai, China).

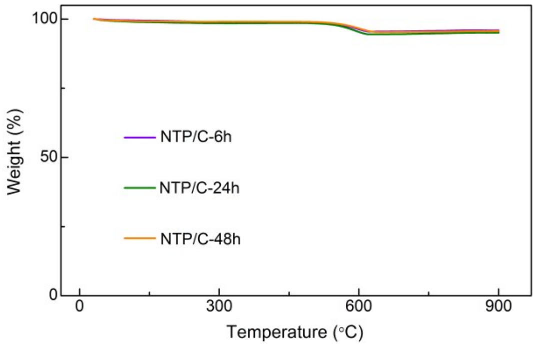

Fig. S1 TGA curves of the NTP/C nanocomposites performed in air condition. The carbon contents of all the NTP/C nanocomposites are at the same level of ~5 wt%.

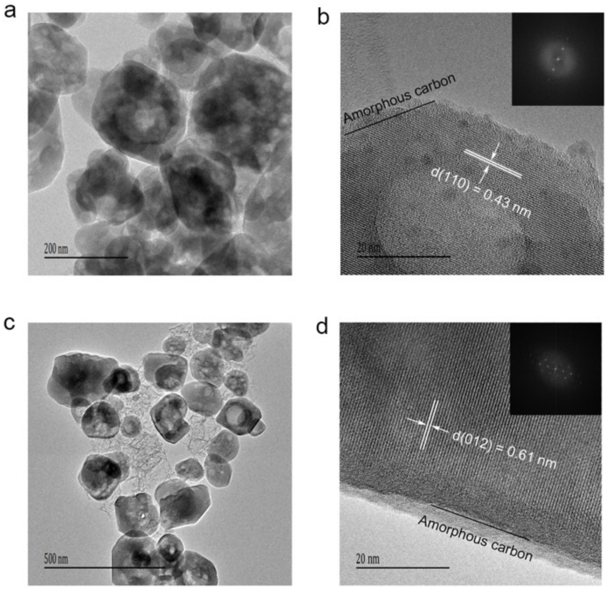

Fig. S2 (a) TEM image of the NTP/C-6h nanocomposite. It manifests the presence of the holes, which are located in the interior of the particles without channels throughout the whole particles. (b) HRTEM image of the NTP/C-6h nanocomposite. The (110) crystal plane in hexagonal NTP and the coated carbon layer are confirmed. The inset is the SAED pattern. (c) TEM image of the NTP/C-48h nanocomposite. The holes also locate in the interior. (d) HRTEM image of the

NTP/C-48h nanocomposite. The (012) crystal plane in hexagonal NTP and the coated carbon layer are confirmed. The inset is the SAED pattern.

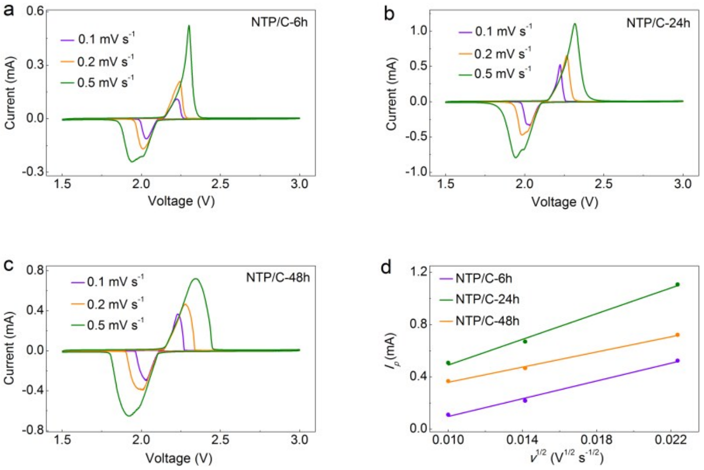

Fig. S3 (a-c) CV curves of the NTP/C-6h, NTP/C-24h, and NTP/C-48h electrodes at various scan rates, respectively. (d) Linear fittings of the peak current as a function of the square root of the scan rate.