Supporting information:

Spatially Confined and Chemical Bonding Amorphous Red Phosphorus into Nitrogen Doped Porous Carbon Tubes Leading to Superior Sodium Storage Performance

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Supplementary videos

Movie S1: The potassiation process for the red P@N-PCTs anode by applying an -1/1 V bias.

Movie S2: The potassiation process for the red P@N-PCTs anode by applying an -6/6 V bias

Supplementary decriptions

Experimental Sections

Preparation of the hollow PPy tubes:

The polycaprolactone (PCL) nanofibers containing with hexadecyl trimethyl ammonium bromide (CTAB) were firstly prepared via the electrospinning method and then directly used as template for the preparation of the hollow polypyrrole (PPy) nanofibers. For the in-situ polymerization of pyrrole monomer on the PCL nanofibers, the as-spun PCL nanofibers film was cut into small squares with a side length of 1cm and then immersed in the aqueous solution of pyrrole under the ice-water bath. The polymerization was initiated with the dropping of the aqueous solution of Ferric chloride ($FeCl_3$) under continuous stirring. With the polymerization of PPy on the surface of the PCL nanofibers film, the color changed from white to black quickly. The obtained PCL@PPy core-shell nanofibers were then washed with deionized water for several times to remove the loosely attached PPy nanoparticles and the residual $FeCl_3$. Finally, the hollow PPy tubes could be obtained with the PCL core dissolved in the DCM solvent.

Preparation of the the nitrogen doped porous carbon tubes (N-PCTs) and the nitrogen doped carbon tubes (N-CTs):

The nitrogen doped porous carbon tubes (N-PCTs) with abundant micropores and ultrahigh surface area could be obtained via the KOH chemical activation process. Firstly, the hollow PPy tubes were immersed in the KOH solution overnight and then dried in an oven at 60 ℃. After then, the PPy tubes were carbonized at 800 ℃ for 0.5 h under argon atmosphere. The N-PCTs sample could be obtained after washed with deionized water for several times and then dried at 60 ℃ in an oven. For comparison, the nitrogen doped carbon tubes (N-CTs) without micropores could be directly fabricated via the carbonization of the hollow PPy tubes at 800 ℃ for 0.5 h under argon atmosphere.

Preparation of the red P@N-PCTs and the red P/N-CTs composite:

The incorporation of red P with the carbon matrix was employed via the vaporization-condensation method as-mentioned in our previous work with the red phosphorus and carbon host mass ratio of 2:1.

Characterization:

The morphology and microstructure were evaluated via the the Field-emission Scanning Electron Microscopy (FESEM) with a JSM-6700 field-emission scanning electron microscope (JEOL, Tokyo, Japan) operated at 5 keV and a JEOL 4000EX Transmission Electron Microscope (TEM) (JEOL, Tokyo, Japan). The crystalline structure were measured via the X-ray Diffraction (XRD, Philips X'pert PRO SUPER) with a Cu Kα radiation and Raman spectroscopy. The surface comparison and chemical bonding states were tested via the X-ray photoelectron spectroscopy (XPS). The specific surface area and the pore diameter were measured via an ASAP 2020 Accelerated Surface Area and Porosimetry instrument.

Electrochemical characterization:

In order to measure the sodium storage capability of the red P@N-PCTs anode, the CR2032 coin cells were assembled with the red P@N-PCTs directly used as the free-standing working electrode and Na metal (purity ≥99.5%, Aladdin) as counter and reference electrode. The assembling of the half-cells was carried in a glove box (MBRAUN LABMASTER 130) filled with high purity argon atmosphere (O_2 and H_2O < 1 ppm). The electrolyte was composed of 1 M $NaClO_4$, ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 w/w), with 5% volume of fluoroethylene carbonate (FEC) as the additives. The glass fiber from Whatman was used as the separator. The charge/discharge performance were measured via the Neware BTS-610 the battery test system. The CHI 660D electrochemical workstation (Chenhua Instrument Company, Shanghai, China) was used to measure the Cyclic voltammetry and electrochemical impedance spectrum (EIS) properties in the frequency range from 100 kHz to 0.01 Hz.

The *in-situ* TEM observation of sodiation/desodiation processes was tested by using the Nanofactory TEM holder operated at 200 kV. The red P@N-PCTs and a piece of Na metal were attached on and mounted to the individual side of the holder with Au and W rods, respectively. Sodiation of an individual red P@N-PCT started when a negative voltage was applied to the Au end, while desodiation initiated upon reversing the sign of the voltage bias. Once the contact between a red P@N-PCT and Na_2O/Na layer was established, a constant bias of −6 V/6 V was applied to the red P@N-PCTs against Na metal to initiate the fast sodiation and desodiation processes.

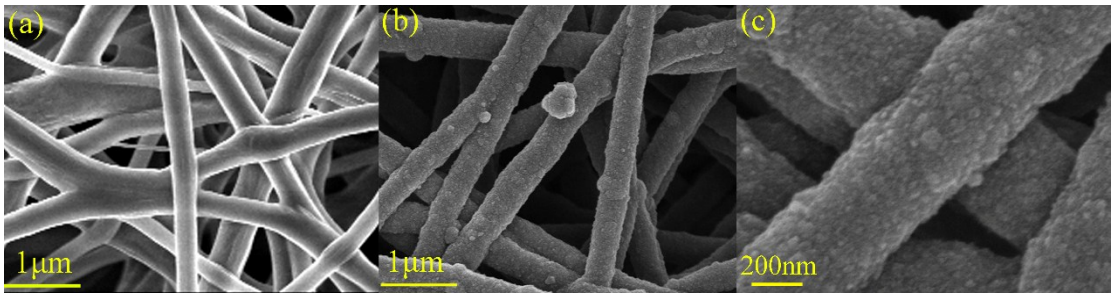

Figure S1. (a) SEM images of the PCL nanofibers; (b-c) SEM images of the PCL@PPy nanofibers.

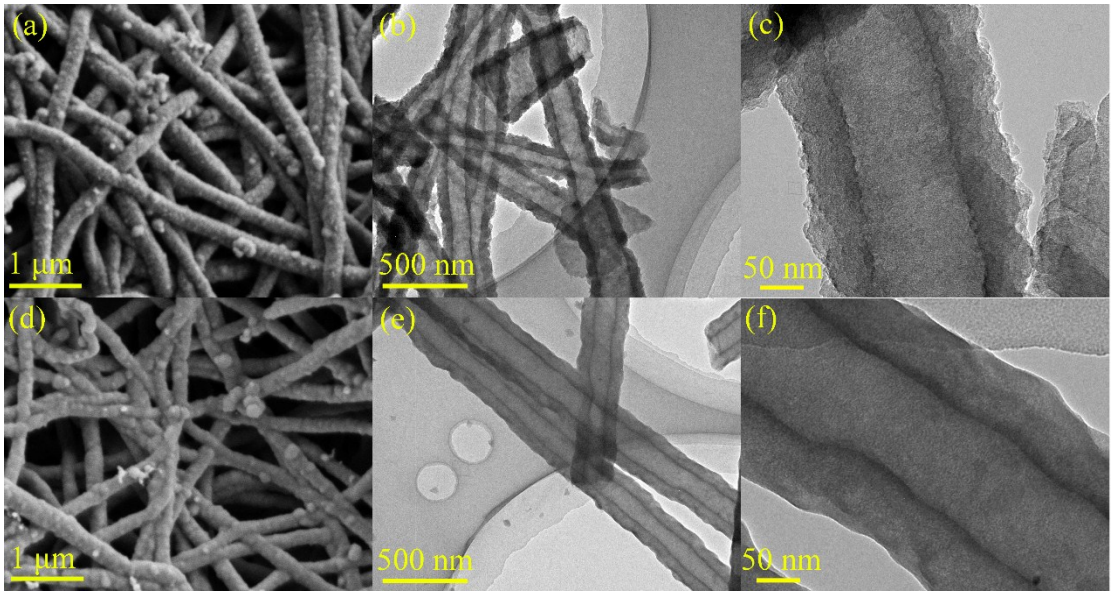

Figure S2. (a-c) SEM and TEM images of the N-CTs; (d-f) SEM and TEM images of the red P/N-CTs.

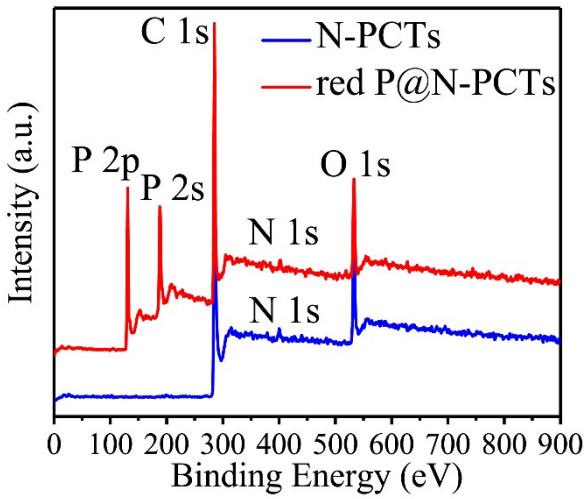

Figure S3. Global XPS profiles of the red P@N-PCTs sample.

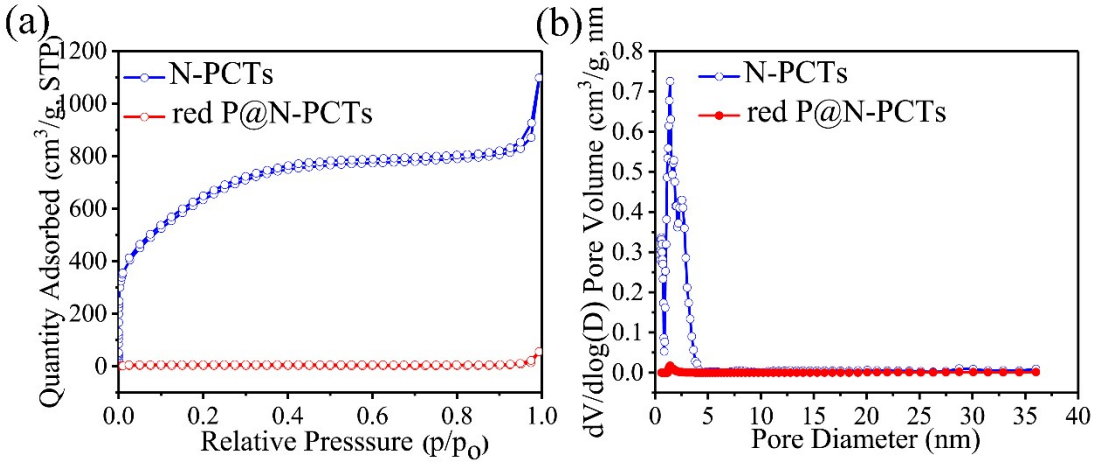

Figure S4. (a-b) N_2 adsorption-desorption isotherms and pore size distributions of the N-PCTs and the red P@N-PCTs.

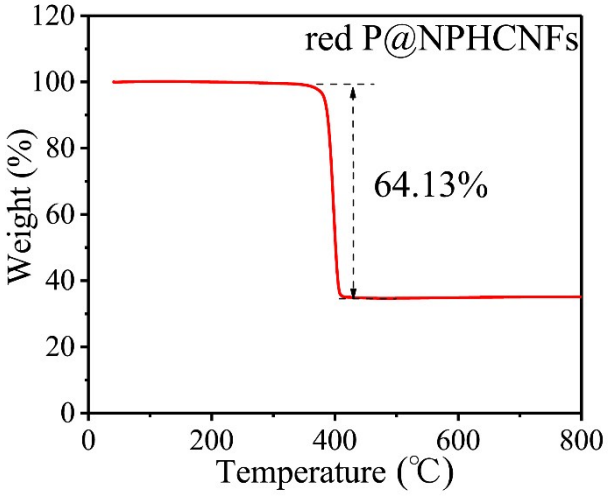

Figure S5. The TGA profile of the red P@N-PCTs sample.