

Supplementary Information

Role of carbon defects in the reversible alloying
states of red phosphorus composite anodes for
efficient sodium ion batteries

*Mengya Li,^a Rachel Carter,^a Landon Oakes,^b Anna Douglas,^b Nitin Muralidharan^b and
Cary L. Pint^{*ab}*

^aDepartment of Mechanical Engineering, Vanderbilt University, Nashville, TN 37235

^bInterdisciplinary Materials Science Program, Vanderbilt University, Nashville, TN
37235

*Corresponding author. Email address: cary.l.pint@vanderbilt.edu

Experimental details

Electrode preparation

The electrode was prepared by hand grinding commercial red phosphorus (red P) (99%, Sigma Aldrich) with single wall carbon nanohorns (SWCNHs) (Carbonium), single wall carbon nanotubes (SWCNTs) (HiPco purified, NanoIntegris), and SWCNT/SWCNH (50%/50%) with a mass ratio of 1:1 for 1h.

Electrochemical test

Pure red P, SWCNH-red P, SWCNT/SWCNH-red P, and SWCNT-red P were mixed with sodium carboxymethyl cellulose (CMC) (Sigma-Aldrich, average Mw ~90,000) as binder and conductive carbon black (TIMCAL, SUPER C45) with a mass ratio of 7:2:1. Then the mixed electrode materials were dissolved in N-methyl-pyrrolidinone (NMP) and sonicated for 1h to form uniform slurry. The slurry was drop-casted onto a stainless steel surface and then dried in vacuum oven at 100 °C overnight. All electrochemical tests were performed in CR 2032 coin-type cells assembled in Ar-filled glovebox. 1 M NaClO₄ (Sigma-Aldrich, ≥98.0%) in ethylene carbonate (EC)/diethyl carbonate (DEC) (Sigma-Aldrich, 99%/>99%) with 1 to 1 volume ratio was used as electrolyte with additional 10 vol% 4-Fluoro-1,3-dioxolan-2-one (FEC) (Alfa Aesar, 98%) as electrolyte additive to help form stable solid-electrolyte interphase (SEI). A Whatman grade GF/F glass fiber microfiber filter (Sigma-Aldrich) was used as separator. Pure sodium was used as counter and reference electrode. Galvanostatic charge/discharge was performed between 0.001 and 2 V at a current density of 200 mA/g_{comp}. Rate studies were performed at current densities of 200, 400, 1000, and 2000 mA/g_{comp}.

Material characterization

Scanning electron microscopy (SEM) images of SWCNH, SWCNT, SWCNH-red P, SWCNT/SWCNH-red P, and SWCNT-red P were acquired by a Zeiss Merlin Scanning Electron Microscope. Raman characterizations were performed by using a Renishaw inVia Raman spectrometer with a 532 nm laser. For characterizations of different alloying products, batteries were immediately opened inside the Ar filled glovebox during 2nd discharging process at different cut-off voltages of 0.30 V, 0.20 V, and 0.001 V, and electrodes were rinsed with DEC solvent carefully before transferring for ex-situ scanning transmission electron microscopy (STEM) study on a FEI Transmission Electron Microscope.

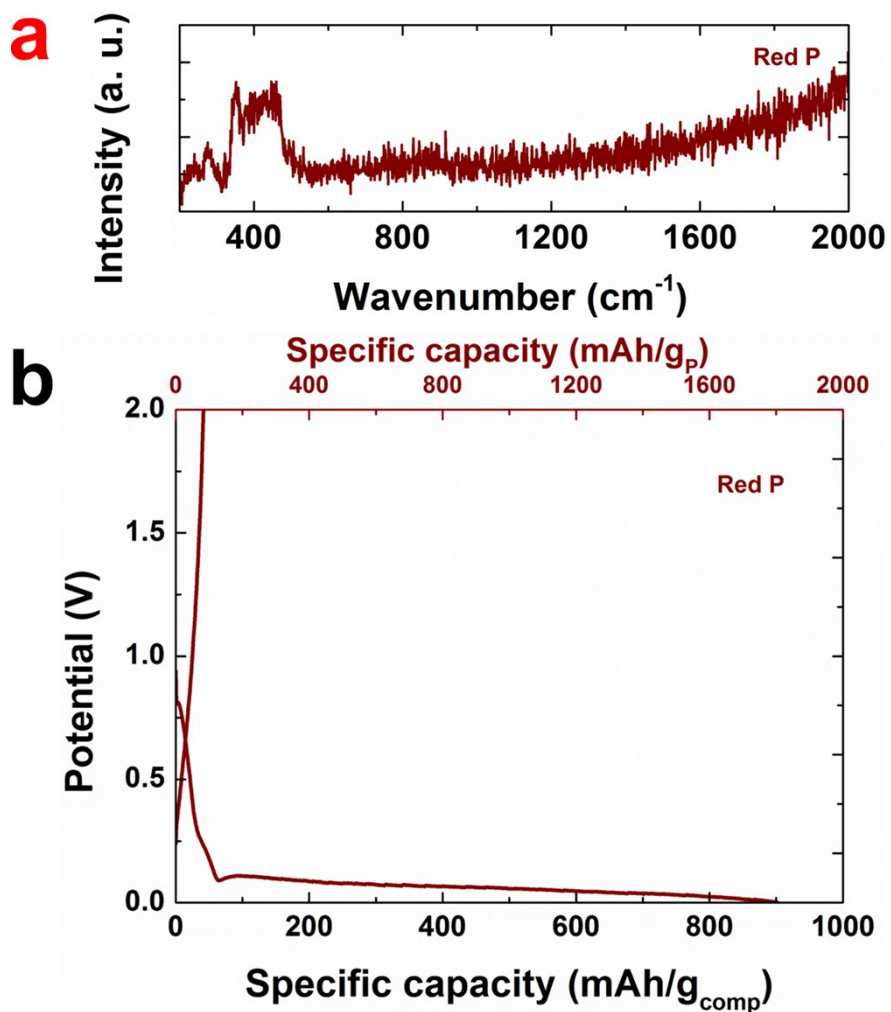


Fig. S1 (a) Raman spectrum of commercial red P; (b) 1st-cycle galvanostatic charge/discharge of pure red P with polymer binder and conductive carbon.

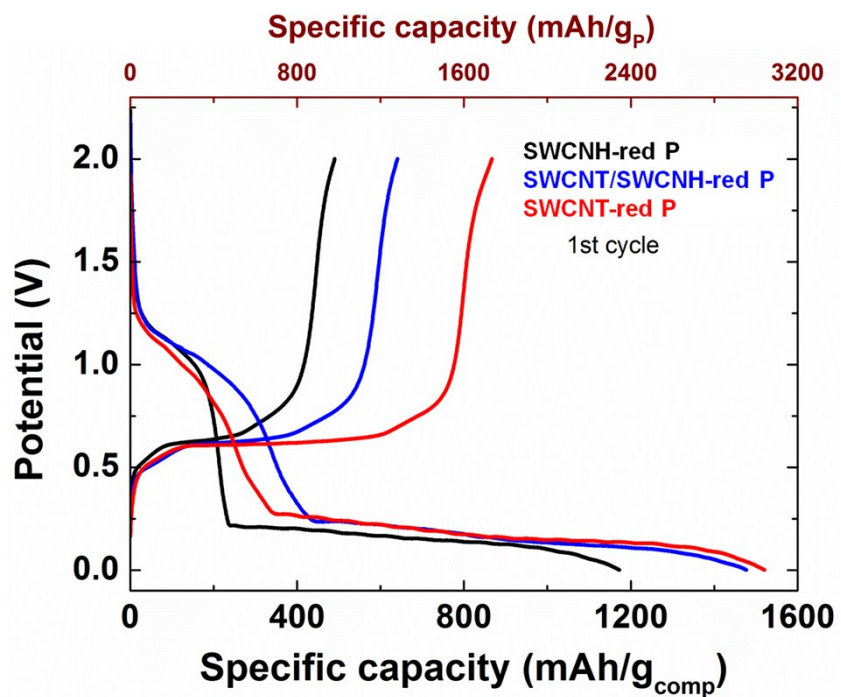


Fig. S2 1st-cycle galvanostatic charge/discharge of SWCNH-red P, SWCNT/SWCNH-red P, and SWCNT-red P.

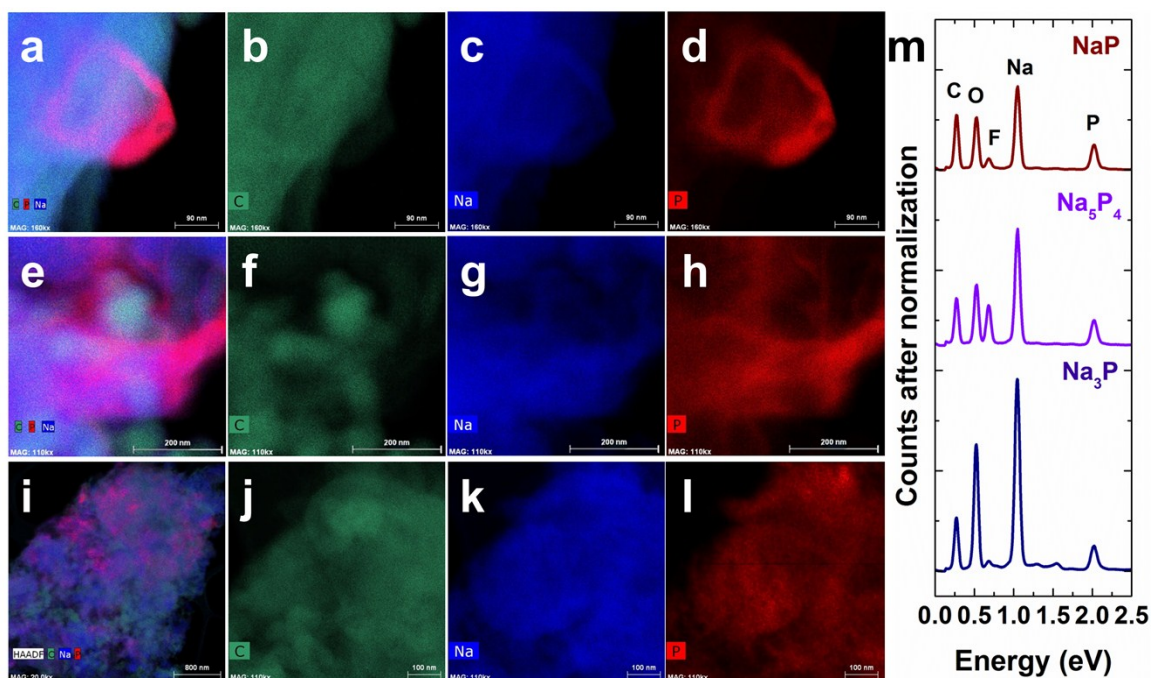


Fig. S3 STEM EDS mapping images of different alloying products of SWCNT-red P anode. (a) to (d): NaP; (e) to (h): Na₅P₄; (i) to (l): Na₃P. (m) STEM EDS elemental spectra of different elements (with little F indicating incomplete electrolyte washing and oxygen indicating brief exposure to air during transferring the sample for TEM).

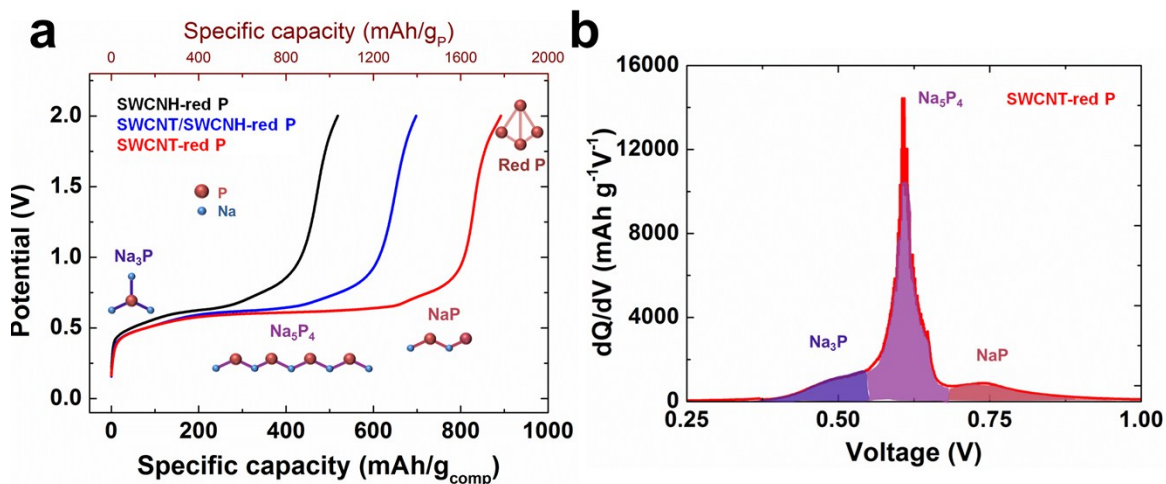


Fig. S4 (a) 2nd-cycle charge comparison with different dealloying phases indicated by car and stick model. (b) dQ/dV curve derived from 2nd charge, with different shading color indicating the capacities delivered by each phase during dealloying.

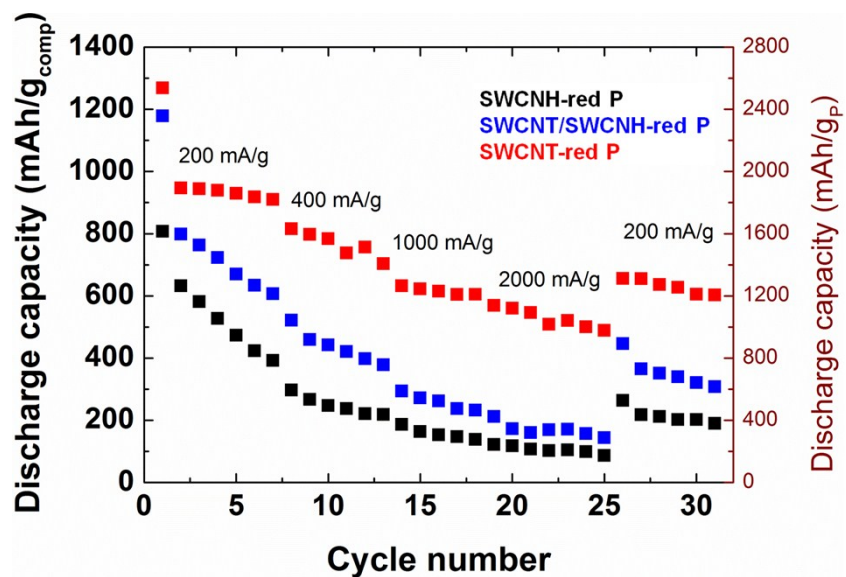


Fig. S5 Rate performance comparison of SWCNH-red P, SWCNT/SWCNH-red P, and SWCNT-red P.