Supporting Information for:

Engineering Tin Phosphides@Carbon Yolk-Shell Nanocube Structures as a Highly Stable Anode Material for Sodium-Ion Batteries

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**Fig. S1.** X-ray diffraction (XRD) patterns of Sn@C and Sn₄P₃@C yolk-shell nanocubes. The XRD pattern of Sn₄P₃@C yolk-shell nanocubes is in good agreement with the standard JCPDS card (No. 73-1820).
Fig. S2. Morphology and composition characterizations of Sn₄P₃/C and bare Sn₄P₃ as the control samples. (a) TEM image and (c) XRD pattern of Sn₄P₃/C material. (b) TEM image and (d) XRD pattern of bare Sn₄P₃.
Fig. S3. X-ray photoelectron spectra (XPS) result of Sn$_4$P$_3$@C yolk-shell nanocubes. (a) Survey XPS of Sn$_4$P$_3$@C yolk-shell nanocubes and (b) the XPS result at Sn 3d$_{5/2}$ region. The survey XPS discloses the co-existence of C, Sn and P elements. The Sn 3d$_{5/2}$ region suggests the preparation of Sn$_4$P$_3$.

Fig. S4. Raman spectrum of the Sn$_4$P$_3$@C yolk-shell nanocubes, revealing the existence of carbon material with moderate graphitic degree.
Fig. S5. Surface area and pore size characteristics of Sn₄P₃@C yolk-shell nanocubes. (a) N₂ adsorption-desorption isotherm and (b) pore size distribution of Sn₄P₃@C yolk-shell nanocubes.

Fig. S6. CV curves of Sn₄P₃@C yolk-shell nanocubes at the scan rate of 0.2 mV s⁻¹ within the potential range of 0.01–2.0 V vs. Na/Na⁺.
**Fig. S7.** *Ex-situ* XRD patterns of the Sn₄P₃@C yolk-shell nanocube electrodes at different charge/discharge states: (a) fresh electrode, (b) after first discharge to 0.5 V, (c) after first discharge to 0.01 V, (d) after first charge to 0.5 V, and (e) after first full charge to 2.0 V.

**Fig. S8.** Morphology of Sn₄P₃@C yolk-shell nanocubes after the electrochemical tests. (a,b) TEM images of Sn₄P₃@C yolk-shell nanocubes after cycling at 2.0 A g⁻¹, showing that the Sn₄P₃ particles were thoroughly encapsulated into the carbon nanocubes, indicating the highly structural integrity.