This ESI for *J. Mater. Chem. A*, 2017, 5, 16994-17000, originally published on 21<sup>st</sup> July 2017, was updated on 17<sup>th</sup> December 2018. The order of Fig. S2-S4 has been changed; the fitting curve was added to Fig. S4, an error in the Y-axis label of Fig. S5b has been corrected and the Y-axis scale adjusted.

## **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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## Figure S1-S8



Fig. S1. X-ray diffraction (XRD) patterns of Sn@C and  $Sn_4P_3@C$  yolk-shell nanocubes. The XRD pattern of  $Sn_4P_3@C$  yolk-shell nanocubes is in good agreement with the standard JCPDS card (No. 73-1820).



**Fig. S2**. Morphology and composition characterizations of  $Sn_4P_3/C$  and bare  $Sn_4P_3$  as the control samples. (a) TEM image and (c) XRD pattern of  $Sn_4P_3/C$  material. (b) TEM image and (d) XRD pattern of bare  $Sn_4P_3$ .



**Fig. S3**. X-ray photoelectron spectra (XPS) result of  $Sn_4P_3@C$  yolk-shell nanocubes. (a) Survey XPS of  $Sn_4P_3@C$  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  $Sn_4P_3$ .



Fig. S4. Raman spectrum of the  $Sn_4P_3@C$  yolk-shell nanocubes, revealing the existence of carbon material with moderate graphitic degree.



Fig. S5. Surface area and pore size characteristics of  $Sn_4P_3@C$  yolk-shell nanocubes. (a)  $N_2$  adsorption-desorption isotherm and (b) pore size distribution of  $Sn_4P_3@C$  yolk-shell nanocubes.



**Fig. S6**. CV curves of  $Sn_4P_3@C$  yolk-shell nanocubes at the scan rate of 0.2 mV s<sup>-1</sup> within the potential range of 0.01–2.0 V *vs.* Na/Na<sup>+</sup>.



**Fig. S7**. *Ex-situ* XRD patterns of the  $Sn_4P_3@C$  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  $Sn_4P_3@C$  yolk-shell nanocubes after the electrochemical tests. (a,b) TEM images of  $Sn_4P_3@C$  yolk-shell nanocubes after cycling at 2.0 A g<sup>-1</sup>, showing that the  $Sn_4P_3$  particles were thoroughly encapsulated into the carbon nanocubes, indicating the highly structural integrity.