Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.
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Supporting Information

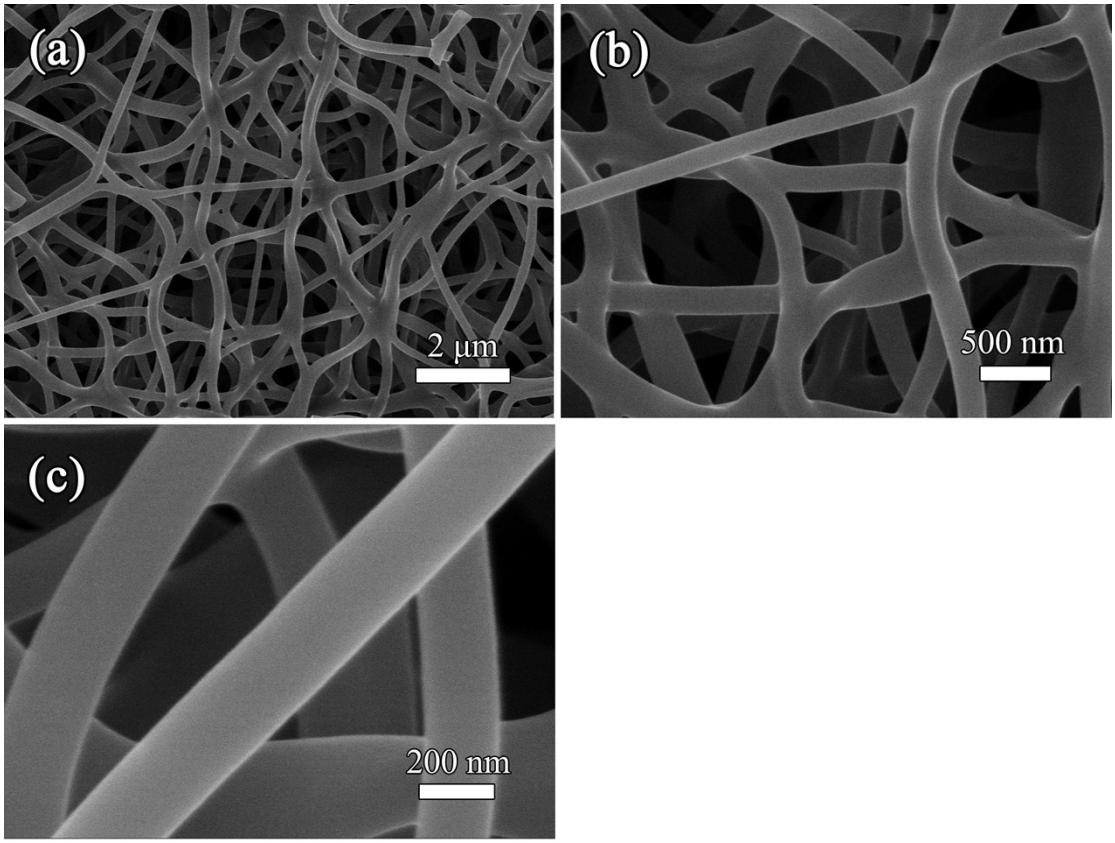

Fig. S1. (a-c) SEM image of N-doped carbon nanofibers (NCNFs)

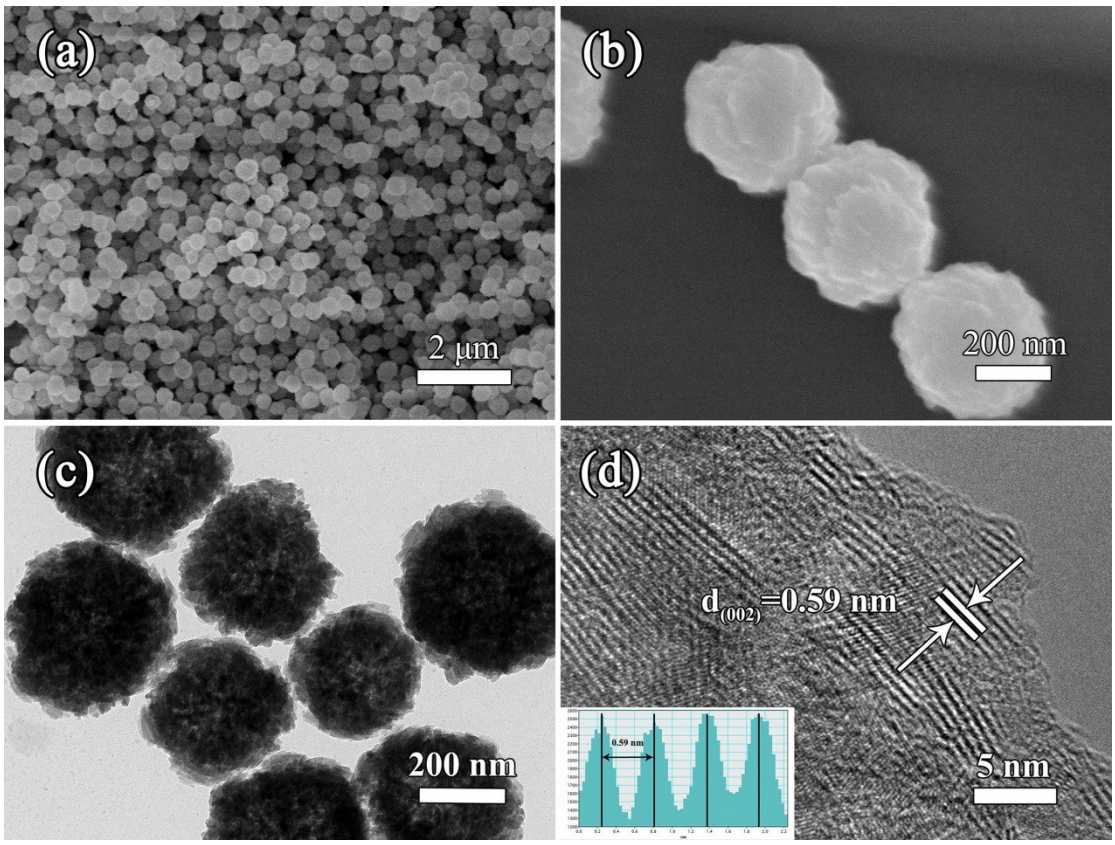

Fig. S2. (a, b) SEM images and (c,d) TEM images of VS_4 microspheres.

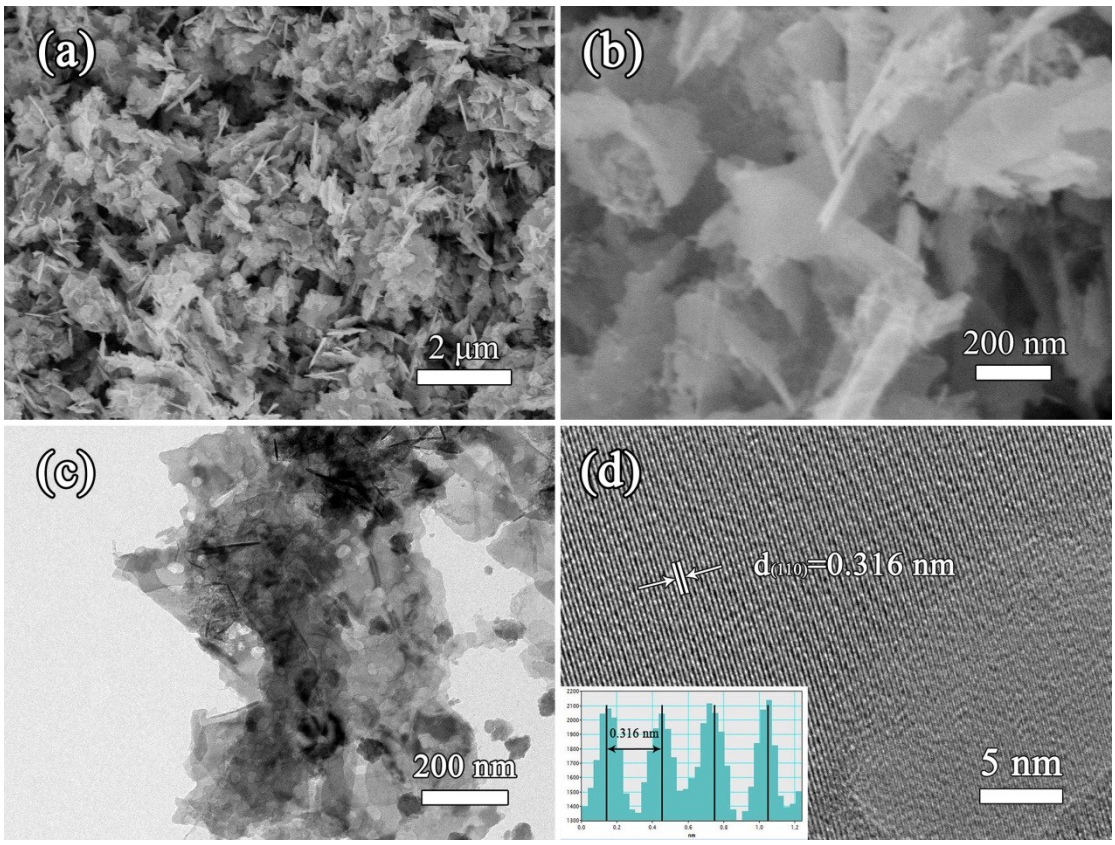

Fig. S3. (a, b) SEM images and (c,d) TEM images of bare V_3S_4 nanosheets.

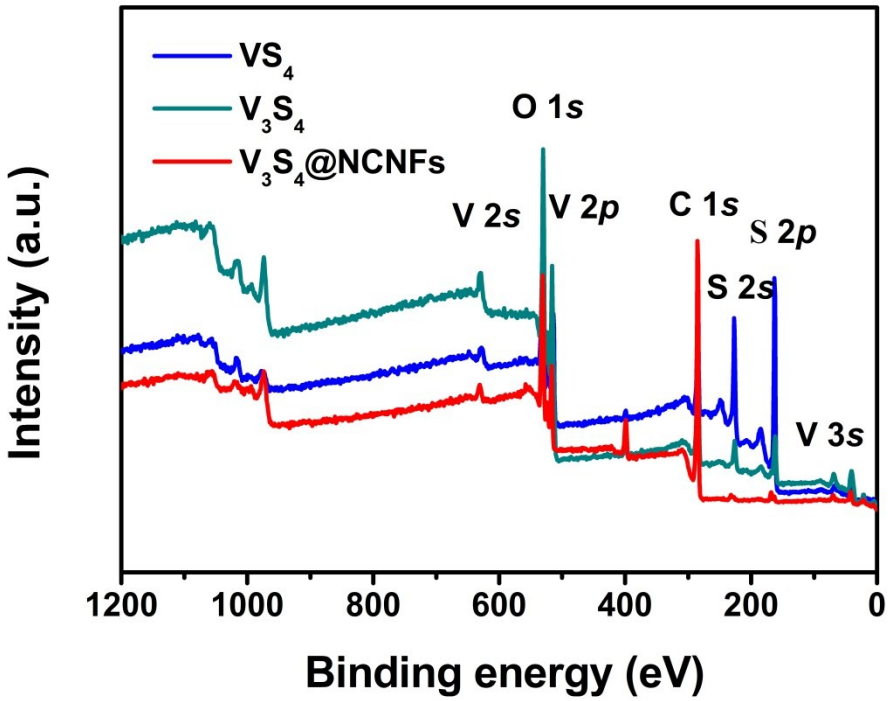

Fig. S4. XPS survey spectrum of VS_4, bare V_3S_4, and V_3S_4@NCNFs composites.

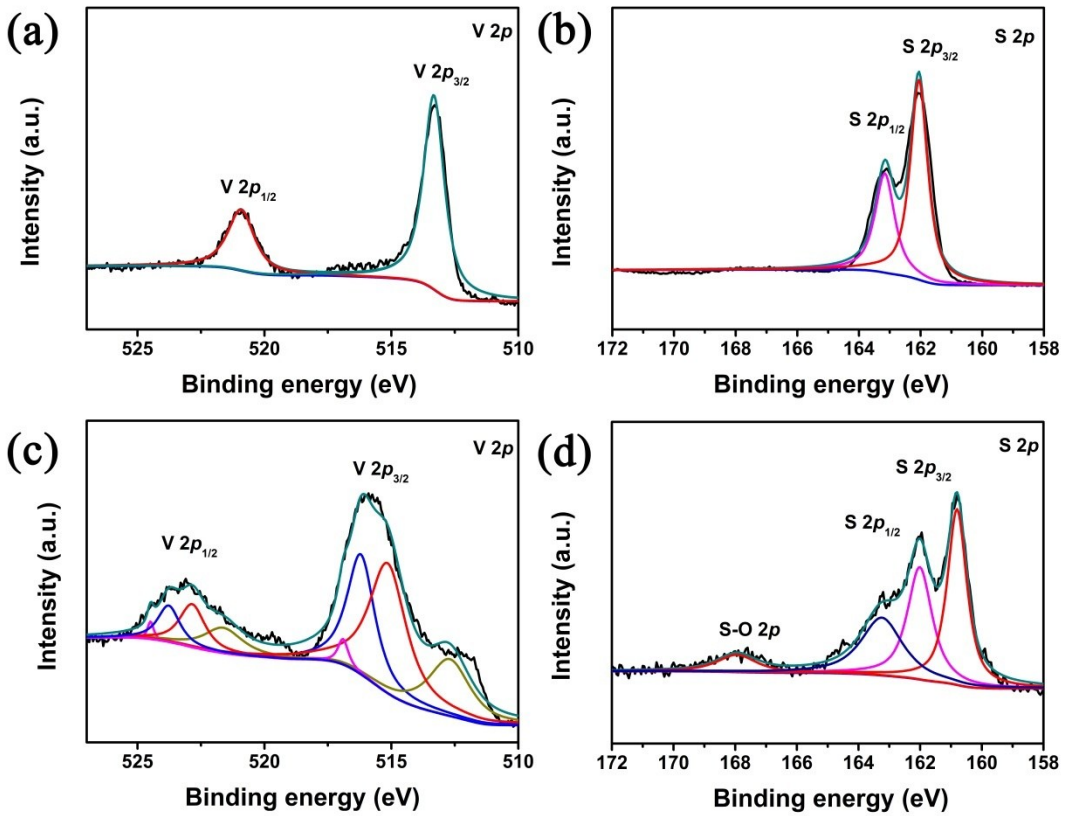

Fig. S5. The high-resolution XPS spectra of VS_4 (a, b), bare V_3S_4 (c, d) with V 2*p*, S 2*p*, respectively.

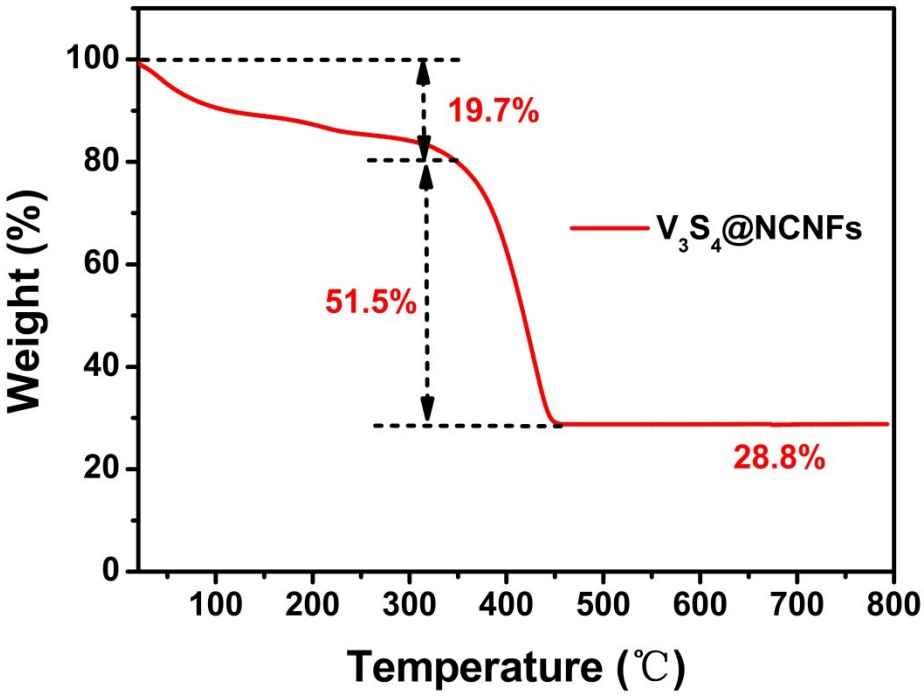

Fig. S6. TGA curves of V_3S_4@NCNFs sample in air from room temperature to 800 °C.

The initial mass loss below 350 °C is ascribed to the oxidation of V_3S_4 into V_2O_5 and the evaporation of water, and the distinct weight loss between 350 and 450 °C could be attributed to the carbon combustion with O_2 into CO_2. The mass ratios of V_3S_4 in these composites are calculated:

$$V_3S_4 + O_2 \rightarrow V_2O_5$$

$$V_3S_4(wt\%) = 100 \times \frac{2 \times M\,V_3S_4}{2 \times M\,V_2O_5} \times \frac{m\,V_2O_5}{m\,V_3S_4@NCNFs}$$

$$= 29.7\%$$

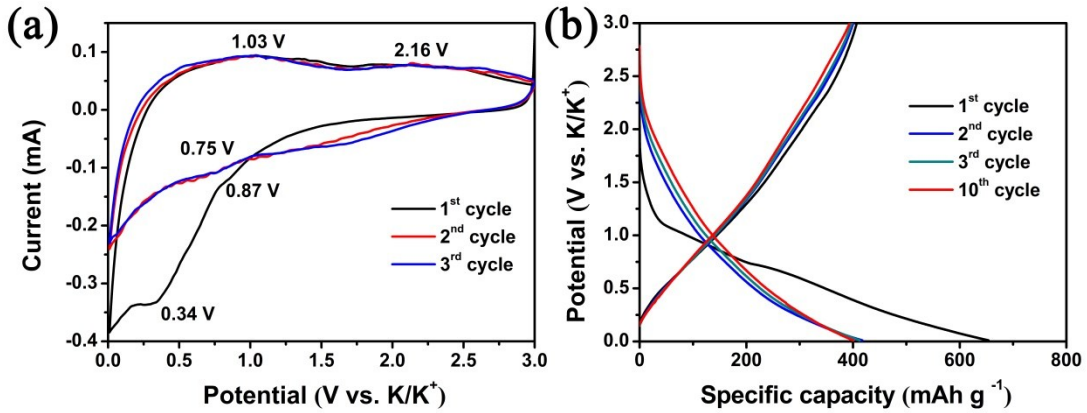

Fig. S7. (a) CV curves of V_3S_4@NCNFs electrode at a scan rate of 0.2 mV s^{-1} in the potential of 0.01-3.0 V (vs. K/K^+). (b) Galvanostatic charge/discharge profiles of V_3S_4@NCNFs at a current density of 0.2 A g^{-1} for PIBs.

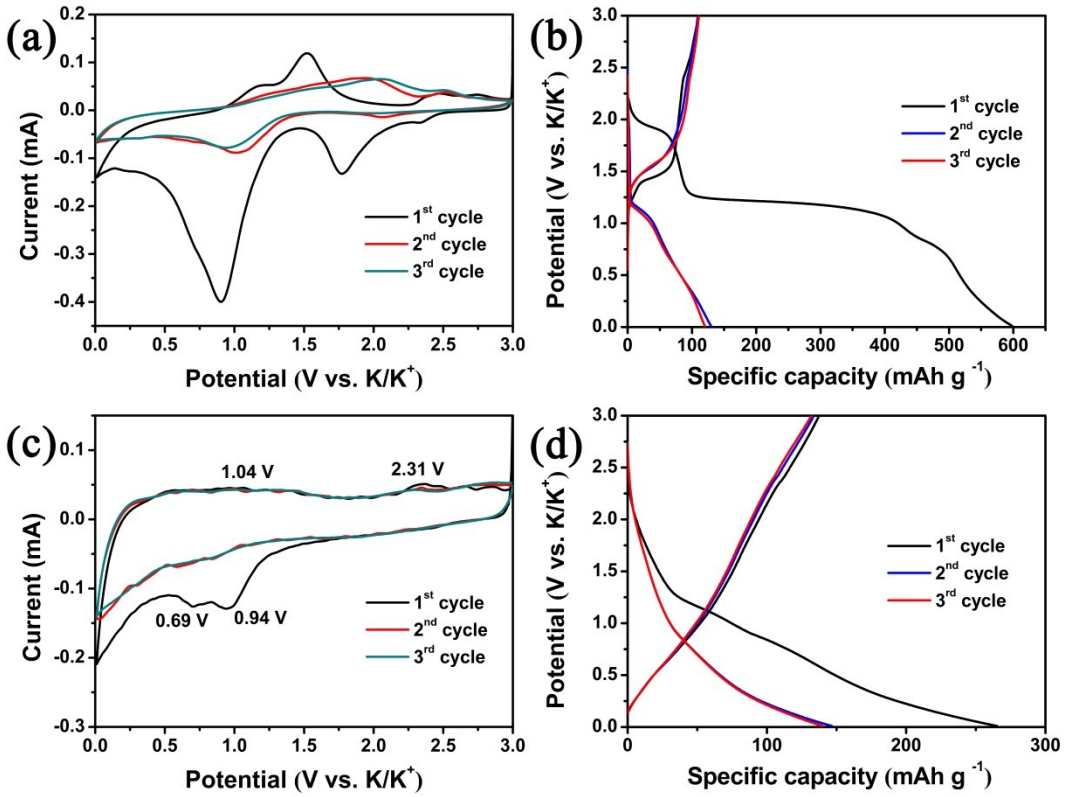

Fig. S8. The CV curves and Galvanostatic charge/discharge profiles of VS_4 (a, b), bare V_3S_4 (c, d), respectively.

The CV curve of VS_4 quite disagree with that of V_3S_4@NCNFs, which have strong cathodic/anodic peaks, in matching with the charge-discharge plateaus of VS_4, which demonstrate its obvious diffusion behavior not pesoducapacitive behavior. Regrettably, there is a large area loss for the CV curves from the first to the second cycle, demonstrating the poor reversibility for VS_4 as the anode in PIBs. The CV image of bare V_3S_4 is similar to that of V_3S_4@NCNFs, which agrees with the charge-discharge weak plateaus of V_3S_4. However, in the subsequent cycle, the V_3S_4 electrode shows the higher potentials of oxidation peaks and lower potentials of corresponding reduced peaks, indicating the large polarization for the potassium extraction/insertion process.[1, 2]

Table S1. Electrochemical performance comparison of vanadium-based and layered transition metal chalcogenides anode materials for PIBs.

Materials	Cycling Performance			Rate performance		Reference
	Discharge Capacity (mAh g^{-1})	Cycles	Current (mA g^{-1})	Discharge Capacity (mAh g^{-1})	Current (A g^{-1})	
V_3S_4@NCNFs	**447** **245**	**300** **1000**	**200** **2000**	**449, 410, 374, 346, 309, 249 and 202**	**0.1, 0.2, 0.5, 1.0, 2.0, 5.0 and 10**	**This work**
VS_2 NSA	410 360	60 100	100 500	400, 380, 330, 250 and 100	0.1, 0.2, 0.5, 1.0 and 2.0	36
V_5S_8@C	501 190	100 1000	50 2000	550, 474, 422, 360, 312, 274, 205 and 153	0.05, 0.1, 0.2, 0.5, 1.0, 2.0, 5.0 and 10	37
VSe_2	335	200	200	374, 350, 334, 269 and 172	0.1, 0.2, 5, 1 and 2.0	53
VN-QDS	228 215	100 500	100 500	261, 215, 187 and 152	0.1, 0.5, 1 and 2.0	54
V_2O_3@PNCNFs	230	200	50	240, 221, 202, 186, 170 and 134	0.05, 0.1, 0.2, 0.3, 0.5 and 1	55
V_2O_{3-x}@rGO	162 104	500 2000	200 1000	250, 210, 175, 160, 127 and 104	0.025, 0.05, 0.1 0.2, 0.5 and 1.0	56
MoS_2/N-doped-C	212 151	200 1000	100 500	258, 238, 204, 171 and 131	0.1, 0.2, 0.5, 1 and 2	38
MoS_2@rGO	416.7 424.6	200 1000	100 500	438.5, 364.8, 302.9, 253 and 196.8	0.1, 0.2, 0.5, 1 and 2	29
WS_2	102.8	100	100	109, 99, 86, 74, 68 and 62	0.05, 0.1, 0.2, 0.4, 0.6 and 0.8	39

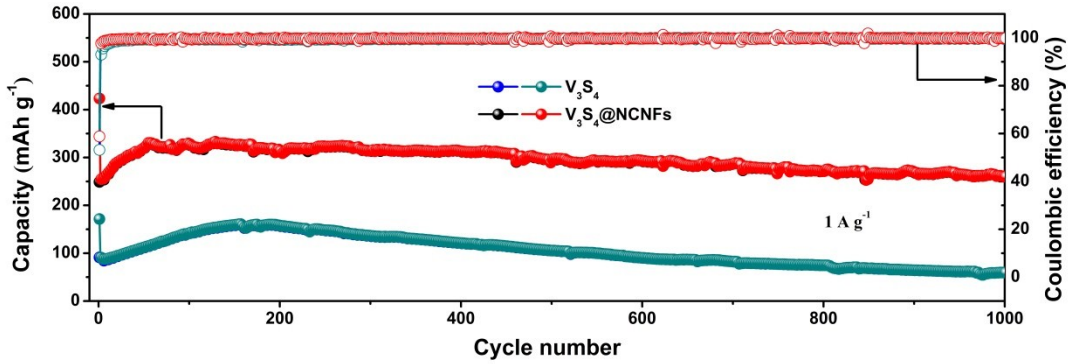

Fig. S9. Long-term cycling stability of the V_3S_4@NCNFs and V_3S_4 electrodes at current densities of 1 A g^{-1}.

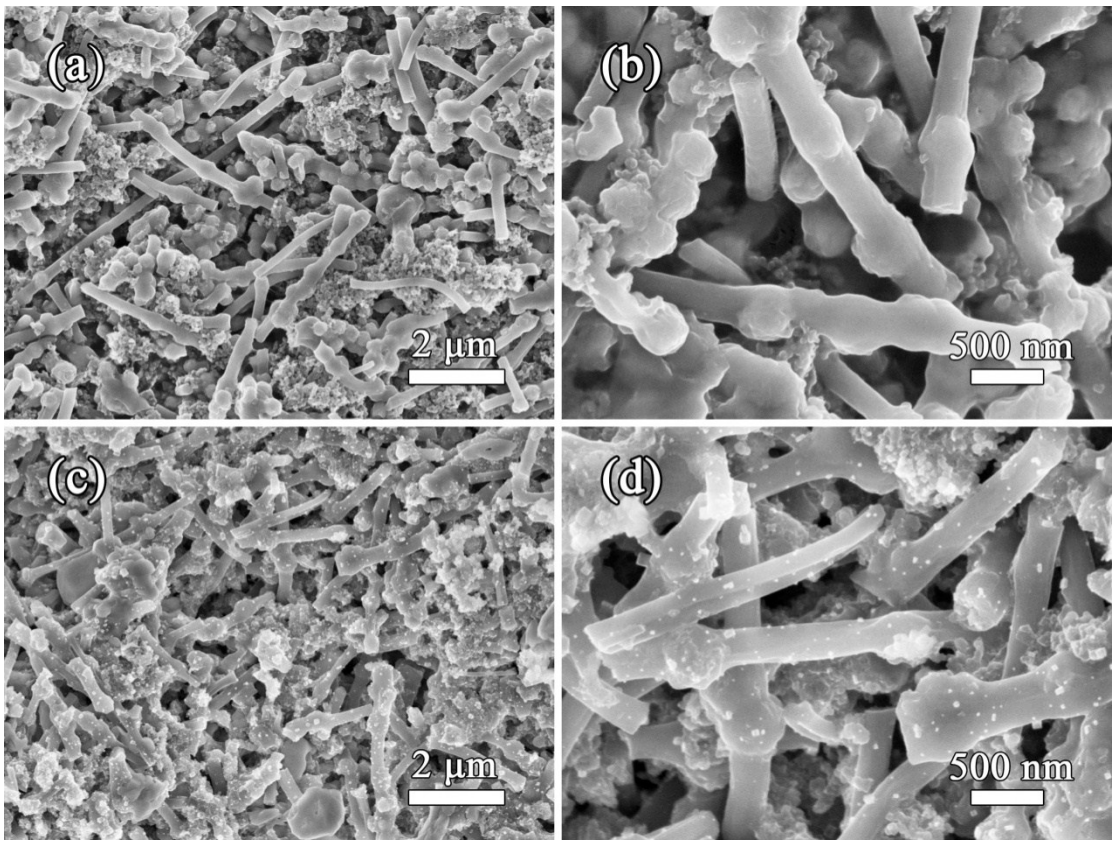

Fig. S10. Different magnifications SEM images of V_3S_4@NCNFs electrode before cycling (a, b) and after 300 cycles at 0.2 A g^{-1}(c, d).

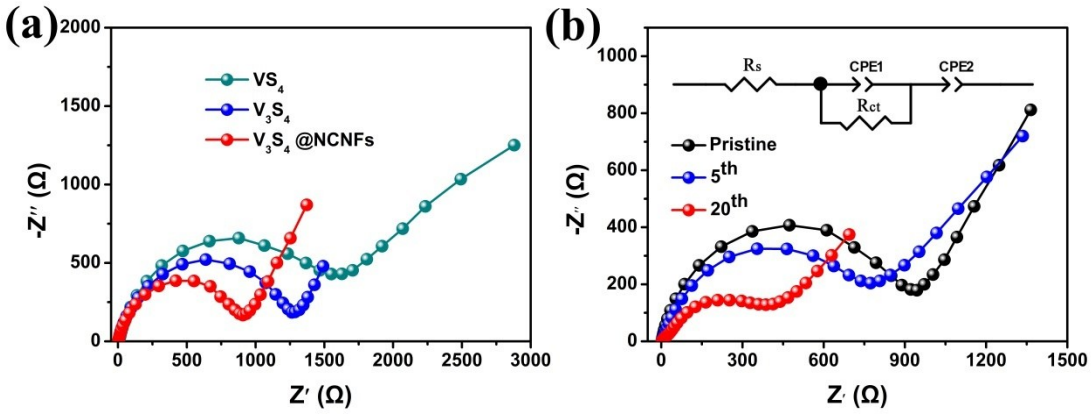

Fig. S11. (a) Nyquist plots of the VS_4, bare V_3S_4, and V_3S_4@NCNFs electrodes. (b) Nyquist plots of the V_3S_4@NCNFs electrodes after different cycles (inset: fitting equivalent circuit).

Table S2. The fitted results of hierarchical V_3S_4@NCNFs based on the equivalent circuit model.

sample	Rs (Ω)	Rct (Ω)
Before cycling	2.41	888
After 5 cycles	2.43	760
After 20 cycles	2.08	493

References

1. C. Mao, Y. Zhong, H. Shang, C. Li, Z. Guo and G. Li, *Chem. Eng. J.*, 2016, **304**, 511-517.
2. D. Zhang, Y. J. Mai, J. Y. Xiang, X. H. Xia, Y. Q. Qiao and J. P. Tu, *J. Power Sources.*, 2012, **217**, 229-235.