## **Supporting Information**

## Oxygen-deficient vanadium oxides@N-doped carbon heterostructure for sodium-ion batteries: insights into charge storage mechanism and enhanced reaction kinetics

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**Fig. S1.** SEM images of the VC product, showing porous spherical morphology with a hierarchical structure.



Fig. S2. Raman spectrum of VNC sample, indicating the presence of carbon species.



**Fig. S3.** (a) Survey and (b) high-resolution O 1s and V 2p XPS spectra of VNC sample.



**Fig. S4**. N<sub>2</sub> adsorption/desorption isotherm curves and pore size distribution plot (inset) of vanadium oxides@N-doped C hybrid sample.



Fig. S5. HRTEM (a) and FFT pattern (b) derived from the dark-yellow square region in (a) of the VNC sample, showing the coexistence of VO and  $V_2O_3$  nanocrystals as marked by green and red, respectively.



**Fig. S6.** Cyclic voltammetry (CV) curves of the VNC (a) and VC (b) electrodes in Na-half cells at  $0.2 \text{ mV s}^{-1}$  in the first three cycles.



**Fig. S7**. Ex-situ XRD pattern of the VNC electrode after discharge, indicating the incomplete conversion reaction of vanadium oxides during discharge.



**Fig. S8.** Optimized geometry structures of Na (a), VO (b), V (c), and Na<sub>2</sub>O (d) on pristine graphene basal plane. The corresponding adsorption energies ( $E_{ads}$ ) and some representative bond lengths (all with unit of Å) are also shown.

	Capacity	Capacity	Capacity	Capacity	Capacity	Capacity
Electrodes	(mAh g <sup>-1</sup> at	(mAh g <sup>-1</sup> at	(mAh g <sup>-1</sup> at	(mAh g <sup>-1</sup> at	(mAh g <sup>-1</sup>	(mAh g <sup>-1</sup>
	0.1 A g <sup>-1</sup> )	0.2 A g <sup>-1</sup> )	0.5 A g <sup>-1</sup> )	1 A g <sup>-1</sup> )	at 2 A g <sup>-1</sup> )	at 5 A g <sup>-1</sup> )
Our work	260	222	204.5	191.6	177.5	166.5
porous	247	202	176	164	149	NA
V <sub>2</sub> O <sub>3</sub> /C <sup>15</sup>						
M-V <sub>2</sub> O <sub>3</sub> <sup>27</sup>	284	242	200	167	136	NA
V <sub>2</sub> O <sub>3</sub> /N-doped	240	233	215	185	170	165
Carbon <sup>26</sup>						(3 A g <sup>-1</sup> )
VO <sub>2</sub> /MX-1 <sup>30</sup>	297	278	265	242	206	NA
			(0.4 A g <sup>-1</sup> )	(0.8 A g <sup>-1</sup> )	(1.6 A g <sup>-1</sup> )	
V <sub>2</sub> O <sub>3</sub> /NG <sup>17</sup>	193	171	150	130	115	NA
HCF-V <sub>2</sub> O <sub>5</sub> <sup>31</sup>	190	146	112	77	NA	NA
TiO <sub>2</sub> @NFG <sup>6</sup>	NA	205	190	170	157	140
		(0.25 A g <sup>-1</sup> )				
TiO <sub>2</sub> /C HRTs <sup>32</sup>	NA	225.6	210.3	191.9	168.6	141
a-Ti <sub>3</sub> C <sub>2</sub> MNRs <sup>33</sup>	108	93	85	NA	NA	NA
			(0.3 A g <sup>-1</sup> )			
Amorphous	250	205	138	100	81	NA
Carbon <sup>34</sup>	(0.06 A g <sup>-</sup>	(0.3 A g <sup>-1</sup> )	(1.2 A g <sup>-1</sup> )	(2.4 A g <sup>-1</sup> )	(4.8 A g <sup>-1</sup> )	

 Table S1. Electrochemical performance comparison of our sample with some

representative anode materials for SIBs in recent literature.

	<sup>1</sup> )					
1D CNF <sup>35</sup>	NA	272	221	183	145	117
					(2.5 A g <sup>-1</sup> )	

NA: not available

	Capacity	Capacity	Capacity	Refs
Electrodes	(mAh g <sup>-1</sup> at 1 A g <sup>-1</sup> for 1	(mAh g <sup>-1</sup> at 1 A g <sup>-1</sup> for 1000	retention	
	cycle)	cycles)	rate(%)	
Our work	214	152	71	This work
porous	181	133	73.5	15
V <sub>2</sub> O <sub>3</sub> /C	(2 A g <sup>-1</sup> )	(2 A g <sup>-1</sup> for 1000 cycles)		
V <sub>2</sub> O <sub>3</sub> /N-	180.9	134.5	74.4	26
doped		(3000 cycles)		
carbon				
VO <sub>2</sub> /MX-1	185.5	143.0	77.1	30
		(200 cycles)		
HCF-V <sub>2</sub> O <sub>5</sub>	368	184	50	31
	$(0.1 \text{ A g}^{-1})$	$(0.1 \text{ A g}^{-1} \text{ for } 100 \text{ cycles})$		
a-Ti <sub>3</sub> C <sub>2</sub>	75	50	66.7	33
MNRs	$(0.2A g^{-1})$	$(0.2 \text{ A g}^{-1} \text{ for 500 cycles})$		
ReS <sub>2</sub> /N-	350	245	70	38
CNFs	(0.1 A g <sup>-1</sup> )	(0.1 A g <sup>-1</sup> for 800 cycles)		
TiO <sub>2</sub> @C	135.4	92.9	68.6	37
nanosheets	(5 A g <sup>-1</sup> )	(5 A g <sup>-1</sup> for 4000 cycles)		
N@S-	520	379	73	36

Table S2. Capacity retention comparison of our sample with some representative

anode materials for SIBs in recent literature.

Carbon	$(0.1 \text{ A g}^{-1})$	$(0.1 \text{ A g}^{-1} \text{ for } 1000 \text{ cycles})$
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