## **Supporting Information**

Highly reversible and fast sodium storage boosted by improved interfacial and surface charge transfer derived from the synergistic effect of heterostructures and pseudocapacitance in SnO<sub>2</sub>-based anodes

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Fig. S1 (a) XRD pattern and (b) Raman spectrum of graphene oxide.

Synthesis of graphene oxide/Co<sub>3</sub>O<sub>4</sub>: The preparation of graphene oxide/Co<sub>3</sub>O<sub>4</sub> was briefly stated as followed. Graphene oxide (GO) (0.04 g) was put into 40 mL deionized water followed by ultrasonic process for 1 h. Then 0.27 g Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and 15 mL ammonia solution (28 wt%) was mixed with GO suspension by ultrasonic for 1 h. Afterwards the mixture suspension was transferred into a Teflon-lined stainless-steel autoclave, sealed and hydrothermally treated at 180 °C for 24 h. The obtained precipitate was washed with deionized water and ethanol and dried at 80 °C for 10 h.



**Fig. S2** (a) XRD pattern, (b) SEM image, and (c) XPS survey spectra of graphene oxide/Co<sub>3</sub>O<sub>4</sub>. (d) The corresponding Co 2p XPS spectrum of GSC and graphene oxide/Co<sub>3</sub>O<sub>4</sub>. The peaks of 797.3 eV and 781.1 eV are ascribed to Co  $2p_{1/2}$  and Co  $2p_{3/2}$  in GSC and the peaks of 796.4 eV and 780.6 eV are ascribed to Co  $2p_{1/2}$  and Co  $2p_{3/2}$  in graphene oxide/Co<sub>3</sub>O<sub>4</sub>. It is obviously that the two peaks of Co 2p for GSC both shifted to higher binding energies compared to those for graphene oxide/Co<sub>3</sub>O<sub>4</sub>, revealing that the 2p electron in Co is interacting with the adjacent SnO<sub>2</sub> for GSC sample.



**Fig. S3** (a) Cyclic voltammetry (CV) profiles of GS at a scan rate of 0.1 mV s<sup>-1</sup>. (b) Galvanostatic discharge-charge profiles of GS within the potential window of 0.01-3.0 V at a current density of 0.1 A g<sup>-1</sup>.



Fig. S4 Galvanostatic discharge-charge profiles of GSC and GS of the second cycle within the potential window of 0.01-3.0 V at a current density of 0.1 A  $g^{-1}$ .



Fig. S5 The equivalent circuit used for the analysis of the impedance plots.  $R_e$  is the electrolyte resistance and the resistance of the surface film formed on the electrodes.  $R_{ct}$  is charge-transfer resistance,  $Z_w$  is the Warburg impedance related to the diffusion of sodium ions into the bulk electrodes and CPE1 represents the constant phase element.



**Fig. S6** (a) Nitrogen adsorption-desorption isotherms and (b) pore size distributions of GSC and GS.



**Fig. S7** (a) Cyclic voltammetry (CV) profiles of GS at various scan rates with the potential range between 0.01 and 3.0 V. (b) Determination of the *b* value using the relationship between peak current and scan rate. A *b* value of 0.5 or 1.0 represents diffusion-controlled or surface-controlled process, respectively. For the scan rates from 0.2 to 0.6 mV s<sup>-1</sup>, the *b* values for the anodic and cathodic peaks are 0.84 and 0.77, respectively, revealing a primarily surface-controlled process. While increasing the scan rate to 0.6 mV s<sup>-1</sup> and above, the slope is decreased and the *b* values decreased to 0.68 and 0.69 for the anodic and cathodic peaks, respectively, indicating a primarily diffusion-controlled process. (c) Normalized contribution ratio of pseudocapactive (red) and diffusion-controlled (blue) contribution at different scan rates. (d) Pseudocapactive (red) and diffusion-controlled (blue) contribution to charge storage of GS at 0.6 mV s<sup>-1</sup>.



**Fig. S8** Pseudocapacitive (red) and diffusion-controlled (blue) contribution to charge storage for GSC at (a) 1, (b) 5, (c) 10 mV s<sup>-1</sup>, and for GS at (d) 1, (e) 5, (f) 10 mV s<sup>-1</sup>.



**Fig. S9** Ex-situ TEM images of GSC after rate capability test (a) with low resolution and (b) with high resolution.



**Fig. S10** (a) Cyclic voltammetry (CV) profiles of GSC-Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> full cell at a scan rate of 0.1 mV s<sup>-1</sup>. (b) Galvanostatic discharge-charge profiles of GSC-Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> full cell within the potential window of 3.4-0.5 V at various current densities. (c) Rate performance of GSC-Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> full cell at applied various current rates.

**Table S1** The comparison of the electrochemical performance of the GSC electrode inthis work with the state of the art results in previously reported researches on  $SnO_2$ -based systems

Sample		Cycling	g Capa	city (mAh g <sup>-1</sup> )	Rate Capacity (mAh g <sup>-1</sup> )		
	3 <sup>rd</sup>	30 <sup>th</sup>	80 <sup>th</sup>	Current Density	1		
This work	597	520	461	0.1 A g <sup>-1</sup>	$370 (0.5 \text{ A g}^{-1})$	270 (1 A g <sup>-1</sup> )	220 (2 A g <sup>-1</sup> )
SnO <sub>2</sub> - graphene <sup>[1]</sup>	361	325		0.05 A g <sup>-1</sup>	$261~(0.2~{\rm A~g^{-1}})$	$213~(0.4~{\rm A~g^{-1}})$	$192~(0.8~{\rm A~g^{-1}})$
SnO <sub>2</sub> -graphene <sup>[2]</sup>	300	275	250	0.02 A g <sup>-1</sup>	$360 (0.2 \text{ A g}^{-1})$	$290~(0.5~{\rm A~g^{-1}})$	$200 (1 \text{ A g}^{-1})$
SnO <sub>2</sub> -C <sup>[3]</sup>	340	310	310	0.1 A g <sup>-1</sup>	190 (0.4 A g <sup>-1</sup> )	$144 (0.8 \mathrm{A  g^{-1}})$	107 (1.6 A g <sup>-1</sup> )
SnO <sub>2</sub> -C <sup>[4]</sup>	800	400	300	0.05 A g <sup>-1</sup>	$449~(0.2~{\rm A~g^{-1}})$	$284~(0.5~{\rm A~g^{-1}})$	$150 (1 \text{ A g}^{-1})$
SnO2@PAIN <sup>[5]</sup>	240	180	190	0.3 A g <sup>-1</sup>	150 (0.4 A g <sup>-1</sup> )	115 (0.8 A g <sup>-1</sup> )	110 (1 A g <sup>-1</sup> )
SnO <sub>2</sub> -rGO <sup>[6]</sup>	360	410	400	0.05 A g <sup>-1</sup>	307 (0.2 A g <sup>-1</sup> )	256 (0.8 A g <sup>-1</sup> )	200 (1.6 A g <sup>-1</sup> )
SnO <sub>2</sub> -N/graphene <sup>[7]</sup>	325	305	280	0.02 A g <sup>-1</sup>	$220 \ (0.16 \ {\rm A \ g^{-1}})$	$190~(0.32~{\rm A~g^{-1}})$	$170~(0.64~{\rm A~g^{-1}})$
SnO <sub>2</sub> -graphene <sup>[8]</sup>	580	350	320	0.02 A g <sup>-1</sup>	299 (0.16 A g <sup>-1</sup> )	$257 (0.32 \text{ A g}^{-1})$	$220~(0.64~{\rm A~g^{-1}})$
SnO <sub>2</sub> -C <sup>[9]</sup>	380	300		0.05 A g <sup>-1</sup>	$300 (0.1 \text{ A g}^{-1})$	$260 (0.2 \text{ A g}^{-1})$	$192~(0.5~{\rm A~g^{-1}})$
SnO <sub>2</sub> microfibers <sup>[10]</sup>	510	216		0.02 A g <sup>-1</sup>	$250 \ (0.16 \ {\rm A \ g^{-1}})$	$150 (0.32 \text{ A g}^{-1})$	80 (0.64 A g <sup>-1</sup> )
PCNF@SnO2@C <sup>[11]</sup>	430	378	370	0.05 A g <sup>-1</sup>	$190 \ (0.2 \ {\rm A \ g^{-1}})$	$144 (0.4 \mathrm{A  g^{-1}})$	$107 (0.8 \text{ A g}^{-1})$
SnO <sub>2</sub> -rGO <sup>[12]</sup>	435	440	390	0.1 A g <sup>-1</sup>	$250 (0.2 \text{ A g}^{-1})$	$184 (0.5 \text{ A g}^{-1})$	121 (1 A g <sup>-1</sup> )
SnO <sub>2</sub> -graphene <sup>[13]</sup>	353	302	287	0.1 A g <sup>-1</sup>	$275 (0.2 \text{ A g}^{-1})$	$250 (0.4 \mathrm{A  g^{-1}})$	221 (0.8 A $g^{-1}$ )
SnO2 <sup>[14]</sup>	498	475	446	0.02 A g <sup>-1</sup>	$370 (0.04 \text{ A g}^{-1})$	250 (0.08 A g <sup>-1</sup> )	221 (0.16 A g <sup>-1</sup> )
SnO2-graphene <sup>[15]</sup>	531	498	486	0.08 A g <sup>-1</sup>	$302 (0.16 \text{ A g}^{-1})$	278 (0.32 A g <sup>-1</sup> )	$126~(0.64~{\rm A~g^{-1}})$
C/SnO <sub>2</sub> /CC <sup>[16]</sup>	500	430	360	0.1 C	422 (1 C)	<b>391</b> (5 C)	342 (10 C)
Al <sub>2</sub> O <sub>3</sub> /SnO <sub>2</sub> /CC <sup>[16]</sup>	450	405	400	0.1 C	<b>331</b> (1 C)	239 (5 C)	89 (10 C)
SnO <sub>2</sub> -C <sup>[17]</sup>	440	400	400	0.5C	298 (1 C)	202 (2 C)	121 (5 C)
SnO <sub>2</sub> @MWCNT <sup>[18]</sup>	479	400		0.1 C	400 (0.2C)	280 (0.5C)	/
SnO <sub>2</sub> /carbon <sup>[19]</sup>	680	539		0.02 A g <sup>-1</sup>	$305 (0.18 \text{ A g}^{-1})$	150 (0.54 A g <sup>-1</sup> )	108 (1.2 A g <sup>-1</sup> )
SnO <sub>2</sub> -N/graphene <sup>[20]</sup>	504	345		0.05 A g <sup>-1</sup>	$252 (0.2 \text{ A g}^{-1})$	$238 (0.4 \mathrm{A  g^{-1}})$	210 (0.8 A g <sup>-1</sup> )
SnO <sub>2</sub> nanowires <sup>[21]</sup>	220	201	$\square$				
SnO <sub>2</sub> /graphene <sup>[22]</sup>	348	320	$\square$	0.05 A g <sup>-1</sup>	$262~(0.2~{\rm A~g^{-1}})$	$201~(0.4~{\rm A~g^{-1}})$	150 (0.8 A g <sup>-1</sup> )
SnO <sub>2</sub> -C <sup>[23]</sup>	380	295	290	0.1 A g <sup>-1</sup>	<b>332</b> (0.2 A g <sup>-1</sup> )	290 (0.5 A g <sup>-1</sup> )	215 (1 A g <sup>-1</sup> )
C@SnO <sub>2</sub> @C <sup>[24]</sup>	$\sim$	$\sim$	$\smallsetminus$		368 (0.25 A g <sup>-1</sup> )	317 (0.5 A g <sup>-1</sup> )	263 (1 A g <sup>-1</sup> )

Sample	$R_{ct}(\Omega)$	σ
GSC	60.13	27.96
GS	130.28	81.96

 Table S2 Kinetic parameters of the GSC and GS electrodes after first reversible
 sodium storage.

 Table S3 Surface area and total pore volume of GSC and GS.

Sample	Surface area (m <sup>2</sup> g <sup>-1</sup> )	Total pore volume (cm <sup>3</sup> g <sup>-1</sup> )		
GSC	189	0.15		
GS	209	0.15		

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