## Supporting Information for

## Smart hybridization of Sn<sub>2</sub>Nb<sub>2</sub>O<sub>7</sub>/SnO<sub>2</sub>@3D carbon nanocomposites with enhanced sodium storage performance through self-buffering effects

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Fig. S1 Typical crystal structure of  $Sn_2Nb_2O_7$  looking from the crystal direction of [101].

From Fig S1, we can clearly observe the arrangement of Sn, Nb, O atoms. The Sn atoms are surrounded by the green NbO<sub>6</sub> octahedra while the Nb and Sn distribute uniformly in the whole crystal. <sup>[S1]</sup> After the first discharge process, the crystal structure becomes amorphous because of the insertion of Na<sup>+</sup> but the Sn, Nb and O will still maintain a uniform distribution.



Fig. S2 XRD pattern of SnO<sub>2</sub>/3DC







Fig. S4 (a) Low-magnified SEM image of as-synthesized  $SnO_2/Sn_2Nb_2O_7@3DC$ ; (b) EDX spectrum of red wire frame area in (a).



Fig. S5 Typical SEM images of (a, b)  $SnO_2/3DC;$  (c, d)  $Nb_2O_5/3DC$  and (e, f)  $SnO_2/Nb_2O_5/3DC.$ 



Fig. S6 (a) XPS survey scan of  $SnO_2/Sn_2Nb_2O_7@3DC$  hybrids; (b) High resolution XPS spectra for C.

From the Fig. S6 (a), we can see that the as-obtained  $SnO_2/Sn_2Nb_2O_7@3DC$  hybrids only contains the elements of Sn, Nb, C and O. In Fig S6 (b), the binding energy peaks located at 284.6, 285.3, 286.3 and 289.2 eV are corresponding to the C-C, C-O, C=O, and O=C-O bonds, respectively. These bonds between C and O come from the residual oxycarbide groups. <sup>[S2]</sup>



Fig. S7 (a) Nitrogen adsorption-desorption isotherms and (b) DFT pore size distribution curve of  $SnO_2/Sn_2Nb_2O_7@3DC$ .



Fig. S8 Galvanostatic discharge/charge profiles of the  $M-Sn_2Nb_2O_7/SnO_2@3DC$  electrode at various current densities of 0.1, 0.2, 0.5, 1.0, 2.0, 5.0, and 10 A g<sup>-1</sup>.

Table S1 Comparison of specific capacity and capacity retention at different current densities for different cycle numbers for  $M-Sn_2Nb_2O_7/SnO_2@3DC$  electrode with other simple composites of  $SnO_2/Carbon$  and  $Nb_2O_5/Carbon$ .

Sample	Current density (A g <sup>-1</sup> )	Specific capacity (mAh g <sup>-1</sup> )	Cycle number	Capacity retention (%)
M-Sn <sub>2</sub> Nb <sub>2</sub> O <sub>7</sub> /SnO <sub>2</sub> @3DC (this work)	0.1	295	100	97.7
	5.0	130	5000	96.3
G-Nb <sub>2</sub> O <sub>5</sub> nanosheets (ref S3)	0.05	230	30	76.7
	4.0	100	1000	90
SnO <sub>2</sub> -PC (ref S4)	0.1	280.1	250	91.6
	1.6	100	1000	93.4
Nb <sub>2</sub> O <sub>5</sub> @C/rGO-50 (ref S5)	0.125	200	300	80
	1.25	130	500	86.7
Al <sub>2</sub> O <sub>3</sub> /SnO <sub>2</sub> /CC (ref S6)	0.134	375	100	80
Nb <sub>2</sub> O <sub>5</sub> NCs/rGO (ref S7)	0.2	181	100	69.2
a-SnO <sub>2</sub> /GA (ref S8)	0.05	380.2	100	91.7
m-Nb <sub>2</sub> O <sub>5</sub> -C (ref S9)	0.05	175	50	94.6
	0.1	100	300	67
SnO <sub>2</sub> /GNS-SCCO <sub>2</sub> (ref S10)	0.02	280	100	82



Fig. S9 (a, b) Typical SEM images of a M-Sn<sub>2</sub>Nb<sub>2</sub>O<sub>7</sub>/SnO<sub>2</sub>@3DC electrode after 100 electrochemical cycles; (c, d) Typical SEM images of a SnO<sub>2</sub>/3DC electrode after 100 electrochemical cycles.



Fig. S10 (a) Cyclic voltammetry curves of  $\text{SnO}_2@3\text{DC}$  electrode at different scan rate ranging from 0.1 to 1.0 mV<sup>-1</sup>; (b) Plot of  $\log(i)$  vs  $\log(v)$  of anodic peaks (red spheres) and corresponding b-value determination (black lines) according to the power law ( $i = av^b$ ). The b value is 0.73 indicating that the electrochemical reactions of  $\text{SnO}_2@3\text{DC}$  electrode is mainly diffusion-controlled.



Fig. S11 Nyquist plots of  $M-Sn_2Nb_2O_7/SnO_2@3DC$ ,  $SnO_2@3DC$ ,  $Nb_2O_5/3DC$  and mechanical mixing of  $SnO_2/Nb_2O_5/3DC$  electrodes after the rate tests over the frequency range from 100 kHz to 10 mHz.



Fig. S12 Ex-situ XRD patterns obtained at different state of the first discharge-charge process to understand the structural change of  $M-Sn_2Nb_2O_7/SnO_2@3DC$  electrode



Fig. S13 (a) HRTEM image of  $M-Sn_2Nb_2O_7/SnO_2@3DC$  electrode material obtained at the discharged voltage of 0.005V; (b, c) charged voltage of 3.0V and (d) TEM image at the charged voltage of 3.0V.



Fig. S14 (a) TEM image and (b) HRTEM image of  $M-Sn_2Nb_2O_7/SnO_2@3DC$  electrode after rate performance test.



Fig. S15 (a) STEM BF image and the corresponding elemental mapping images of (b) carbon; (c) tin; (d) niobium; (e) oxygen and (f) sodium.

## **References:**

S1. Hosogi, Y.; Shimodaira, Y.; Kato, H.; Kobayashi, H.; Kudo, A., *Chem. Mater.*, 2008, 20 (4), 1299-1307.

S2. Chen, B.; Liu, E.; He, F.; Shi, C.; He, C.; Li, J.; Zhao, N., *Nano Energy*, 2016, 26, 541-549.

S3. Wang, L.; Bi, X.; Yang, S., Adv. Mater, 2016, 28 (35), 7672-9.

S4. Huang, Z.; Hou, H.; Zou, G.; Chen, J.; Zhang, Y.; Liao, H.; Li, S.; Ji, X., *Electrochim Acta* 2016, *214*, 156-164.

S5. Lim, E.; Jo, C.; Kim, M. S.; Kim, M. H.; Chun, J.; Kim, H.; Park, J.; Roh, K. C.; Kang, K.; Yoon, S.; Lee, J., *Adv. Funct. Mater.*, 2016, *26* (21), 3711-3719.

S6. Liu, Y.; Fang, X.; Ge, M.; Rong, J.; Shen, C.; Zhang, A.; Enaya, H. A.; Zhou, C., *Nano energy* 2015, *16*, 399-407.

S7. Yan, L.; Chen, G.; Sarker, S.; Richins, S.; Wang, H.; Xu, W.; Rui, X.; Luo, H.,

ACS Appl. Mat. Interfaces, 2016, 8 (34), 22213-22219.

S8. Fan, L.; Li, X.; Yan, B.; Feng, J.; Xiong, D.; Li, D.; Gu, L.; Wen, Y.; Lawes, S.; Sun, X., *Adv. Energy Mater.*, 2016, *6* (10), 1502057.

S9. Kim, H.; Lim, E.; Jo, C.; Yoon, G.; Hwang, J.; Jeong, S.; Lee, J.; Kang, K., *Nano Energy* 2015, *16*, 62-70.

S10. Patra, J.; Chen, H.-C.; Yang, C.-H.; Hsieh, C.-T.; Su, C.-Y.; Chang, J.-K., *Nano Energy* 2016, *28*, 124-134.