Supporting Information for:

## MoO<sub>3</sub>@Ni Nanowire Array Hierarchical Anode for High Capacity and Superior Longevity All-Metal-Oxide Asymmetric Supercapacitors

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Figure S1. SEM images of NNA at (a) low and (b) high magnifications (top view).



Figure S2. Top view SEM image of MoO<sub>3</sub>@NNA electrode.



Figure S3. Side-view SEM images of VO2@NNA at low (a) and high (b) magnification.



**Figure S4.** Morphological study on NNA@VO<sub>2</sub> nanostructure. (a). TEM image of NNA@VO<sub>2</sub> electrode. (b). High resolution image of NNA@VO<sub>2</sub> electrode (inset: FFT diffraction pattern focusing on VO<sub>2</sub> shell). (c). STEM image of a piece of NNA@VO2 nanowire, (d)-(f)



Figure S5. XPS analysis of NNA@VO<sub>2</sub>. (a). V 2p spectrums of NNA@VO<sub>2</sub>. (b) O 1s spectrum of NNA@VO<sub>2</sub>.



**Figure S6.** Electrochemical performance of NNA@VO<sub>2</sub> electrode. (a). CV curves of NNA@VO<sub>2</sub> electrode at different scan rate ranging from 1 mV/s to 100 mV/s. (b). Areal and gravimetric capacitance of NNA@VO<sub>2</sub> at different scan rate. (c). GCD curves of NNA@VO<sub>2</sub> electrode at different current densities. (d). Cycling performance of NNA@VO<sub>2</sub> electrode at a constant current density of 20 mA/cm<sup>2</sup>.



**Figure S7.** Morphological study on NNA@MoO<sub>3</sub> and NNA@VO<sub>2</sub> nanostructures after cycling. (a)-(b) and NNA@VO<sub>2</sub> (c)-(d) electrodes after 20000 GCD cycles.



**Figure S8.** The GCD curves of NNA-ASC for 1<sup>st</sup>, 100<sup>th</sup>, 1000<sup>th</sup>, 5000<sup>th</sup>, 10000<sup>th</sup> and 20000<sup>th</sup> cycles.



Figure S9. Digital images of the as-assembled NNA-AAS for driving an LED during bending test.(a) After bending the NNA-ASC to 90° by hand and releasing. (b) The NNA-AAS was pressed flat after bending.



**Figure S10.** Ragone plot of NNA-ASC based on the total mass of active materials and area of the supercapacitor unit.

 Table S1. Comparison on areal capacitance and cycling performance on NNA-ASC and recent

 advanced energy storage energy storage devices.

Materials	Maximized	Cycling performance	Ref
	areal/volumetric		
	capacitance		
NF-Bi <sub>2</sub> O <sub>3</sub> //MnO <sub>2</sub> -ASC	97 mF cm <sup>-2</sup> at 1.5 mA cm <sup>-2</sup>	85 % after 4000 cycles	1
MoO <sub>3</sub> /CNT//MnO <sub>2</sub> /CNT ASC	4.9 F cm <sup>-3</sup> at 0.08 A cm <sup>-3</sup>	83 % after 5000 cycles	2
Fe <sub>2</sub> O <sub>3</sub> //MnO <sub>2</sub> ASC	0.131 F cm <sup>-3</sup> at 0.42 mA cm <sup>-3</sup>	97 % after 5000 cycles	3
Ni(OH) <sub>2</sub> NPL symmetric SC	75 mF cm <sup>-2</sup> and 833 F cm <sup>-3</sup> at	76 % after 10000 cycles	4
	50 mV s <sup>-1</sup>		
NNA-based MoO <sub>3</sub> //VO <sub>2</sub> ASC	307 mF cm <sup>-2</sup> and 6.14 F cm <sup>-3</sup> at	116.7 % after 20000 cycles	This
	2 A g <sup>-1</sup>		work

Note. NNA: Ni nanowire arrays; NF: nano-carbon fiber; CNT, carbon nanotubes; NPL: nanoporous layer;

## References

- 1. H. Xu, X. Hu, H. Yang, Y. Sun, C. Hu and Y. Huang, *Advanced Energy Materials*, 2015, 5.
- P. Yang, Y. Chen, X. Yu, P. Qiang, K. Wang, X. Cai, S. Tan, P. Liu, J. Song and W. Mai, *Nano Energy*, 2014, 10, 108-116.
- Q. Lv, S. Wang, H. Sun, J. Luo, J. Xiao, J. Xiao, F. Xiao and S. Wang, *Nano letters*, 2016, 16, 40-47.
- 4. Y. Yang, G. Ruan, C. Xiang, G. Wang and J. M. Tour, *Journal of the American Chemical Society*, 2014, **136**, 6187-6190.