Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A. This journal is © The Royal Society of Chemistry 2018

## Supporting Information

## Few-layered ReS<sub>2</sub> Nanosheets Vertically Aligned on Reduced Graphene Oxide for Superior Lithium and Sodium Storage

Sheng Liu, Yan Liu, Xin Zhou, Kang Xu,\* Qiquan Qiao,\* and Wen-Hua Zhang\*

Dr. S. Liu, Dr. Y. Liu, Prof. W.-H. Zhang Sichuan Research Center of New Materials Institute of Chemical Materials, China Academy of Engineering Physics 596 Yinhe Road, Chengdu 610200, China E-mail: whzhang@caep.cn

Prof. X. ZhouCollege of Environment and Chemical EngineeringDalian University10 Xuefu Street, Dalian 116622, China

Dr. K. Xu lectrochemistry Branch, Sensor and Electron Devices Directorate, Power and Energy Division, U.S. Army Research Laboratory, Adelphi, MD 20783, USA E-mail: conrad.k.xu.civ@mail.mil

Prof. Q. Qiao Center for Advanced Photovoltaics, Department of Electrical Engineering and Computer Sciences South Dakota State University Brookings, SD 57007, USA. E-mail: qiquan.qiao@sdstate.edu



Figure S1. (a, b) SEM and (c, d) TEM images of the pure ReS<sub>2</sub>.



Figure S2. The typical TEM image of GO.



**Figure S3**. (a, b) SEM and (c, d) TEM images of the *v*-ReS<sub>2</sub>/rGO. The ultrathin ReS<sub>2</sub> nanosheets are observed to be ultra-uniformly distributed on rGO.



**Figure S4**. (a) The supplementary HRTEM image and (b) the layer number-distribution histogram of the *v*-ReS<sub>2</sub>/rGO. The average number of ReS<sub>2</sub> layers in the *v*-ReS<sub>2</sub>/rGO is statistically observed to be  $6\pm 2$ .



**Figure S5.** (a-d) SEM and (e, f) TEM images of the *v*-ReS<sub>2</sub>/rGO nanocomposites synthesized without addition of hydroxylamine hydrochloride (HAH).



**Figure S6.** TEM images of the *v*-ReS<sub>2</sub>/rGO synthesized via a two-step hydrothermal process. In the first step, 1.00 mmol of HAH, 3 mL of GO suspension and 12 mL of deionized water were hydrothermally treated at 240 °C for 8 h. The as-prepared powder (*i.e.*, rGO) was then collected by centrifugation and wash. In the second step, a mixture of the as-obtained rGO powders, 0.35 mmol of NH<sub>4</sub>ReO<sub>4</sub>, 1.50 mmol of NH<sub>2</sub>CSNH<sub>2</sub>, and 15 mL of deionized water was hydrothermally treated at 240 °C for 8 h.



**Figure S7.** TG analysis curves of the pure ReS<sub>2</sub>, GO, and *v*-ReS<sub>2</sub>/rGO under air atmosphere at a heating rate of 10 °C min<sup>-1</sup>. For the GO, the weight loss below 227 °C is attributed to the removal of the labile oxygen-containing functional groups and the moisture. In contrast, the *v*-ReS<sub>2</sub>/rGO exhibits an increased thermal stability below 227 °C due to the removal of the labile oxygen-containing functional groups by chemical reduction of the GO. A significant drop in mass above ~326 °C can be ascribed to the oxidation/sublimation of ReS<sub>2</sub>. Therefore, the weight loss between 227 and 326 °C can be considered as the pyrolysis of graphene sheets. That is, the content of graphene in the *v*-ReS<sub>2</sub>/rGO is estimated to be ~9 *wt*.%.



**Figure S8.** (a) the typical N<sub>2</sub> adsorption-desorption isotherm and (b) the corresponding BJH pore size distribution of the *v*-ReS<sub>2</sub>/rGO. The BET specific surface area, total pore volume and BJH average pore size of the *v*-ReS<sub>2</sub>/rGO are 49.6 m<sup>2</sup> g<sup>-1</sup>, 0.23 cm<sup>3</sup> g<sup>-1</sup>, and 3.5 nm, respectively. The porous nature of our v-ReS<sub>2</sub>/rGO composite accommodates the volume change during intercalation/de-intercalation and favors electrolyte penetration, which resulting in the superior cycling and rate capacities of the v-ReS<sub>2</sub>/rGO.

Active material	Current density (mA g <sup>-1</sup> )	Initial charging capacity (mAh g <sup>-1</sup> )	Reversible capacity (mAh g <sup>-1</sup> ) /Cycle number	Reference
Our v-ReS2/rGO	100	871	915/100 <sup>th</sup>	This study
	1000	613	342/500 <sup>th</sup>	
v-ReS <sub>2</sub> /3DGF	1000	~680	200/500 <sup>th</sup>	[1]
<b>ReS2 spheres</b>	86	843	421/30 <sup>th</sup>	[2]
ReS <sub>2</sub> /rGO	86	885	745/50 <sup>th</sup>	[3]
ReS <sub>2</sub> /CNTs	215	847	793/100 <sup>th</sup>	[4]
ReS <sub>2</sub> /N-CNFs	100	630	440/400 <sup>th</sup>	[5]
ReS <sub>2</sub> /CMK-3	500	663	620/200 <sup>th</sup>	[6]

Table S1. Comparison of cycling performances for  $ReS_2$ -based LIB anode materials.



**Figure S9.** LIBs: Nyquist impedance plots of the pure ReS<sub>2</sub>, rGO, and *v*-ReS<sub>2</sub>/rGO (a) in newly assembled cells and (b) after rate capability tests. SIBs: Nyquist impedance plots of the pure ReS<sub>2</sub>, rGO, and *v*-ReS<sub>2</sub>/rGO (c) in newly assembled cells and (d) after rate capability tests. (e) The equivalent circuit model for fitting Nyquist impedance plots. Herein,  $R_s$ ,  $R_f$ ,  $R_{ct}$ ,  $Z_w$  and *CPE* denote the electrolyte resistance, the contact resistance across SEI films, the charge-transfer resistance, the impedance related to the diffusion of lithium ions within the electrode, and a constant phase element of the electrode/electrolyte interface, respectively. The Nyquist impedance plots combine two depressed semicircle in the high and medium frequency region and a straight line in the low-frequency region. The semicircle in medium frequencies is usually associated to the charge-transfer resistance ( $R_{ct}$ ) across the electrode-electrolyte interface. For LIBs and SIBs,  $R_{ct}$  of the *v*-ReS<sub>2</sub>/rGO electrode is significantly smaller than that of the pure ReS<sub>2</sub> and rGO electrodes, manifesting that the intimate contact between rGO and the few layered ReS<sub>2</sub> nanosheets can greatly promote the charge transfer kinetics at the electrodes during the electrode process, thereby leading to an excellence rate capability and cyclability.



**Figure S10**. The typical TEM images of the *v*-ReS<sub>2</sub>/rGO after 100 cycles at a current density of 100 mA g<sup>-1</sup>. The sandwich structure is well kept without any restacks and breaks, indicating the excellent stability of the *v*-ReS<sub>2</sub>/rGO electrode. Figure S12b further reveals that the ReS<sub>2</sub> nanosheets for the *v*-ReS<sub>2</sub>/rGO have been pulverized into tiny nanoparticles (~2 nm), which still ultra-uniformly and closely attached on the surfaces of rGO. These results demonstrate that the sandwich-like structure of *v*-ReS<sub>2</sub>/rGO can efficiently prevent restacking or aggregation of both ReS<sub>2</sub> and rGO during cycling.



**Figure S11**. CV curves for SIBs during the first five cycles at 0.1 mV s<sup>-1</sup>: (a) the v-ReS<sub>2</sub>/rGO, (b) ReS<sub>2</sub> and (c) rGO electrodes. As observed, the CV curves of the v-ReS<sub>2</sub>/rGO (Figure S11a) are nearly an superposed result of ReS<sub>2</sub> (Figure S11b) and rGO (Figure S11c), clearly indicative of the significant synergistic effect between the few-layered ReS<sub>2</sub> and graphene substrate with the sandwich-like structure.





**Figure S12**. The relaxed structures of ReS<sub>2</sub>/GO by DFT calculations and the ralative adsorption energies. The dark gray, green, blue, yellow, red and white spheres represent C, N, Re, and S atoms, respectively. We define the adsorption energies of the perpendicular (a) C-O-Re and (c) C-O-H structure and the parallel (e) C-O-H structure as 0 eV. As a sresult, the relative adsorption energies of the parallel (b) C-O-S and (d) C-O structure and the perpendicular (f) C-Re structure are 0.55, 1.23 and 3.31 eV, respectively. According to the definition, a more positive value of the relative adsorption energy corresponds to more endothermic and weeker adsorption.

## **Supporting References**

- Zhang, Qin, Shuangjie Tan, Rafael G. Mendes, Zhongti Sun, Yongting Chen, Xin Kong, Yinghui Xue, Mark H. Rümmeli, Xiaojun Wu, Shengli Chen, and Lei Fu, Extremely Weak van der Waals Coupling in Vertical ReS<sub>2</sub> Nanowalls for High-Current-Density Lithium-Ion Batteries, *Adv. Mater.*, 2016, 28, 2616-2623.
- Qi, Fei, Yuanfu Chen, Binjie Zheng, Jiarui He, Qian Li, Xinqiang Wang, Bo Yu, Jie Lin, Jinhao Zhou, Pingjian Li, and Wanli Zhang, 3D Chrysanthemum-like ReS<sub>2</sub> Microspheres Composed of Curly Few-layered Nanosheets with Enhanced Electrochemical Properties for Lithium-ion Batteries, *J. Mater. Sci.*, 2017, 52, 3622-3629.
- Qi, Fei, Yuanfu Chen, Binjie Zheng, Jiarui He, Qian Li, Xinqiang Wang, Jie Lin, Jinhao Zhou, Bo Yu, Pingjian Li, and Wanli Zhang, Hierarchical Architecture of ReS<sub>2</sub>/rGO Composites with Enhanced Electrochemical Properties for Lithium-ion Batteries, *Appl. Surf. Sci.*, 2017, 413, 123-128.
- [4] Qi, Fei, Jiarui He, Yuanfu Chen, Binjie Zheng, Qian Li, Xinqiang Wang, Bo Yu, Jie Lin, Jinhao Zhou, Pingjian Li, Wanli Zhang, and Yanrong Li, Few-layered ReS<sub>2</sub> Nanosheets Grown on Carbon Nanotubes: A Highly Efficient Anode for High-performance Lithium-ion Batteries, *Chem. Eng. J.*, 2017, 315, 10-17.
- [5] Mao, Minglei, Chunyu Cui, Mingguang Wu, Ming Zhang, Tao Gao, Xiulin Fan, Ji Chen, Taihong Wang, Jianmin Ma, and Chunsheng Wang, Flexible ReS<sub>2</sub> Nanosheets/N-doped Carbon Nanofibers-Based Paper as a Universal Anode for Alkali (Li, Na, K) Ion Battery, *Nano Energy*, 2018, 45, 346-352.
- [6] Wang, Huijun, Xia Yang, Yaqin Chai, Sheng Liu, and Ruo Yuan, Ultrathin ReS<sub>2</sub> nanosheets growing on ordered microporous carbon for high capacity lithium ion batteries, *J. Alloys Compd.*, **2018**, 767, 204-209.