

Supporting Information

Superior Sodium Storage of Novel VO₂ Nano-microspheres Encapsulated into Crumpled Reduced Graphene Oxide

Bo Yan,^{a, c} Xifei Li,^{*b, c} Zhimin Bai,^{*a} Liangxu Lin,^d Gang Chen,^e Xiaosheng Song,^c
Dongbin Xiong,^c Dejun Li,^c Xueliang Sun^{f, c}

^a*Beijing Key Laboratory of Materials Utilization of Nonmetallic Minerals and Solid Wastes, National Laboratory of Mineral Materials, School of Materials Science and Technology, China University of Geosciences, Beijing 100083, China. E-mail: zhimibai@cugb.edu.cn; Tel: +86-13691115187*

^b*Center for Advanced Energy Materials and Devices, Xi'an University of Technology, Xi'an 710048, China. E-mail: xfli2011@hotmail.com; Tel: +86-13502042013*

^c*Tianjin International Joint Research Centre of Surface Technology for Energy Storage Materials, College of Physics and Materials Science, Tianjin Normal University, Tianjin 300387, China.*

^d*College of Engineering, Mathematics and Physical Sciences, University of Exeter, Exeter, EX44QL, UK*

^e*School of Physical Science and Technology, ShanghaiTech University, Shanghai 201210, China.*

^f*Nanomaterials and Energy Lab, Department of Mechanical and Materials Engineering, University of Western Ontario, London, Ontario N6A 5B9, Canada. E-mail: xsun@eng.uwo.ca*

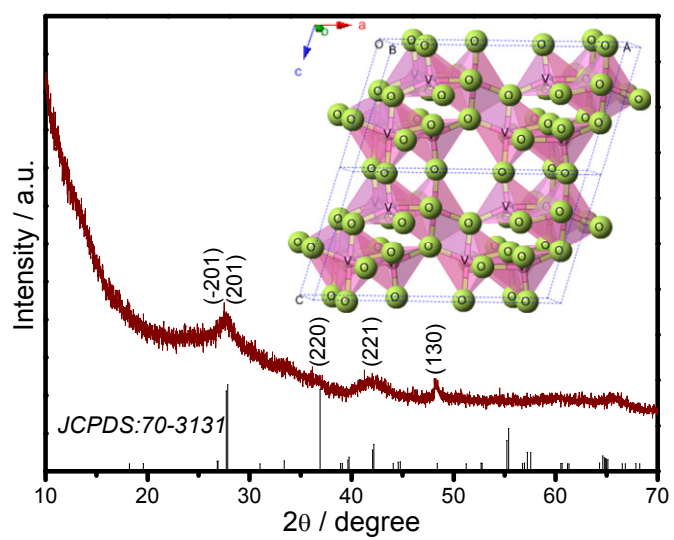


Fig. S1 XRD patterns for cG/VO₂. Inset shows the crystalline structure of monoclinic VO₂(B).

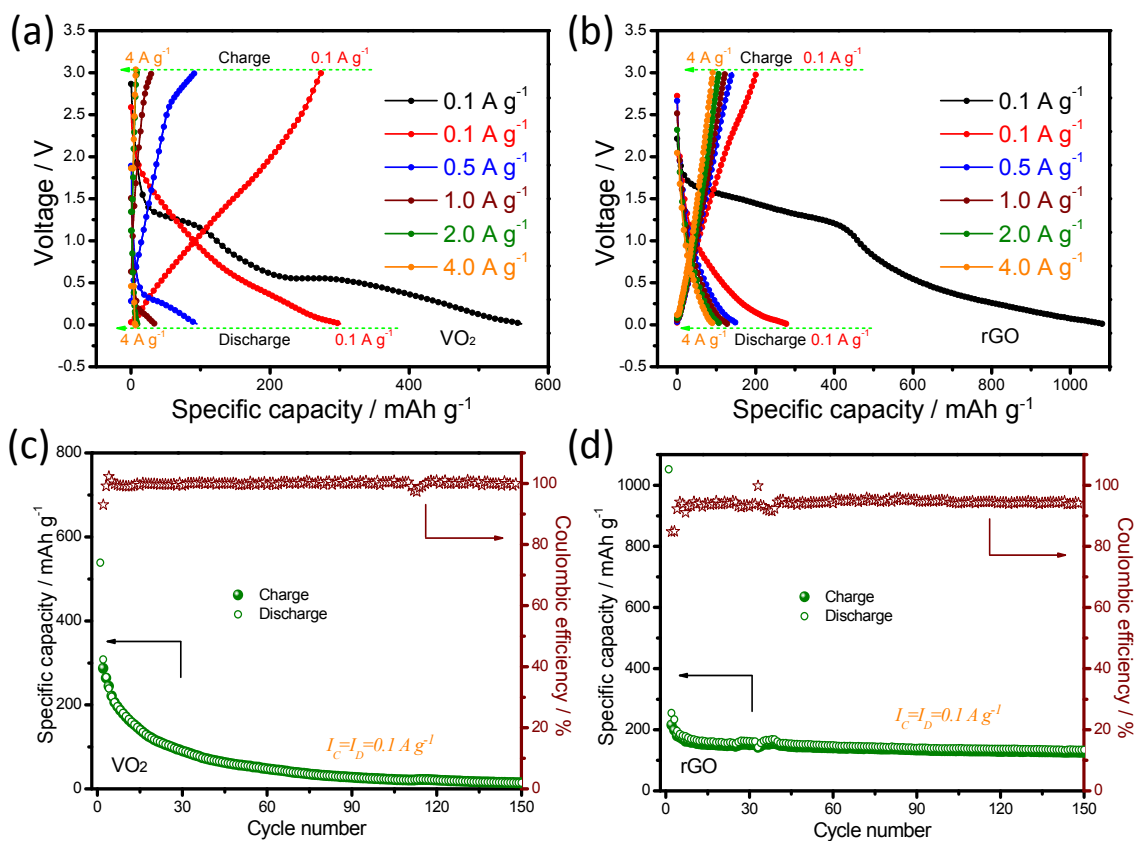


Fig. S2 Electrochemical properties of the prepared materials: Galvanostatic charge/discharge voltage profiles at various current densities of the (a) pristine VO₂ and (b) rGO. Cycling performance and Coulombic efficiency of the (c) pristine VO₂ and (d) rGO electrode at a current density of 0.1 A g⁻¹.

Table S1. The summarization of as-prepared cG/VO₂ and the VO₂ anode previously reported in the literature.

VO ₂ materials	Synthetic method	Voltage range	Current density	The third discharge capacity (mAh g ⁻¹)	Capacity retention (%)	Rate capacity (mAh g ⁻¹) at relevant current density	Ref.
rGO/VO ₂ nanorods (10 wt%/90 wt%)	Microwave-assisted solvothermal	0.25 ~ 3.0 V	60 mA/g	220	82.7 (after 200 cycles)	100 at 0.8 A/g	[1]
cG/VO ₂ (10.5 wt% /89.5 wt%)	Solvothermal	0.01 ~ 3.0 V	100 mA/g	378	84.2 (after 200 cycles)	307 at 1 A/g; 214 at 4 A/g	Ours

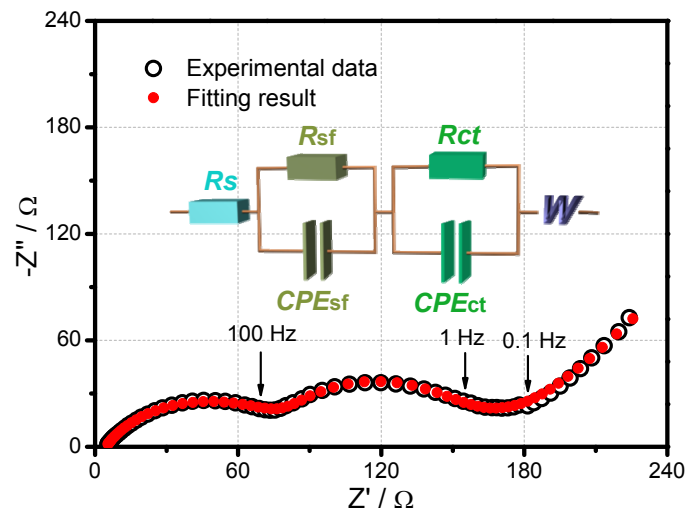


Fig. S3 The typical fitting data of Nyquist plot for cG/VO₂ anode discharged to 0.01 V in the 2nd cycle.

Table S2. Typical fitting parameters of cG/VO₂ anode discharged to 0.01 Vin the 2nd cycle.

Electrolyte	R_e	4.576 Ω
SEI	R_{sf}	80.29 Ω
	CPE_{sf-T}	5.3306E-05
	CPE_{sf-P}	0.6943
Charge transfer	R_{ct}	55.84 Ω
	CPE_{ct-T}	4.2153E-04
	CPE_{ct-P}	0.9734
Diffusion	R_d of W_{dif}	113.7 Ω
	T of W_{dif}	2.561
	P of W_{dif}	0.3026

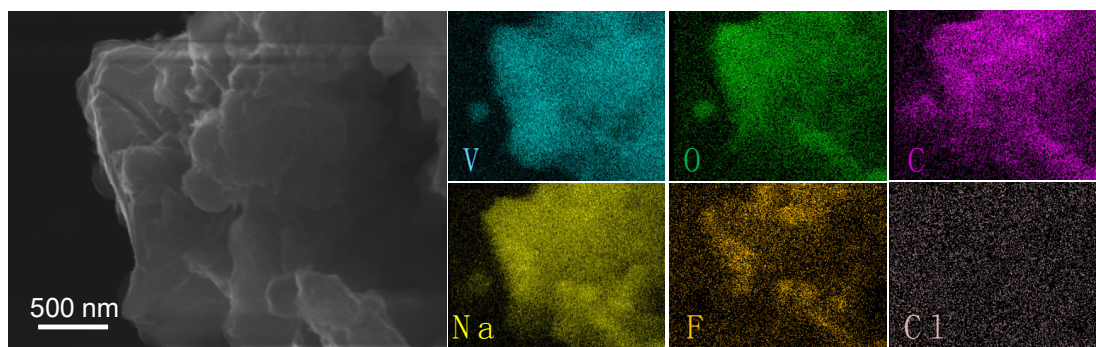


Fig. S4 Elemental mapping of the cG/VO₂ electrode discharged to 1.6 V in the 2nd cycle. The intensity of chlorine map can be served as a contrastive benchmark.

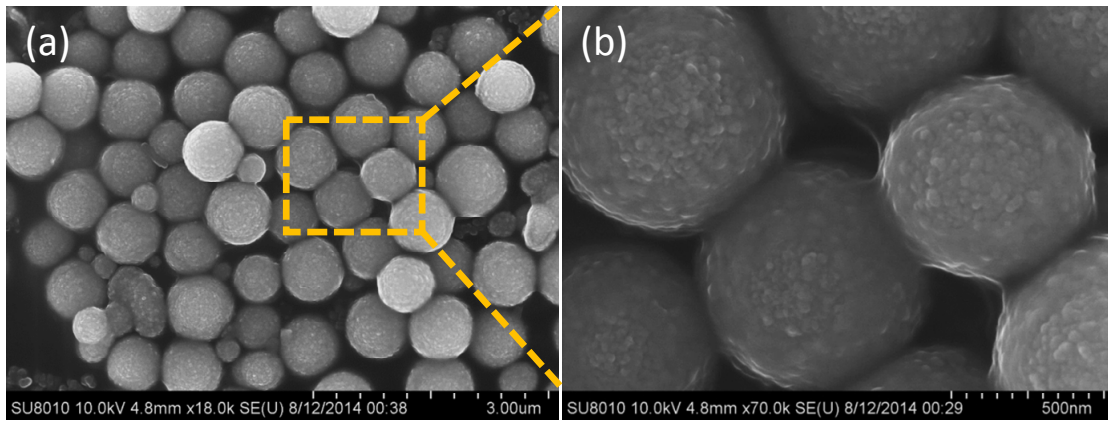


Fig. S5 (a) Low- and (b) high-magnification FESEM images of the reduced graphene oxide and VO₂ composite prepared with 3 mL of VOCl₂ solution (0.11 M) and 1.5 mL of GO ethylene glycol dispersion (2 mg mL⁻¹) at 200 °C after solvothermal reaction for 8h.

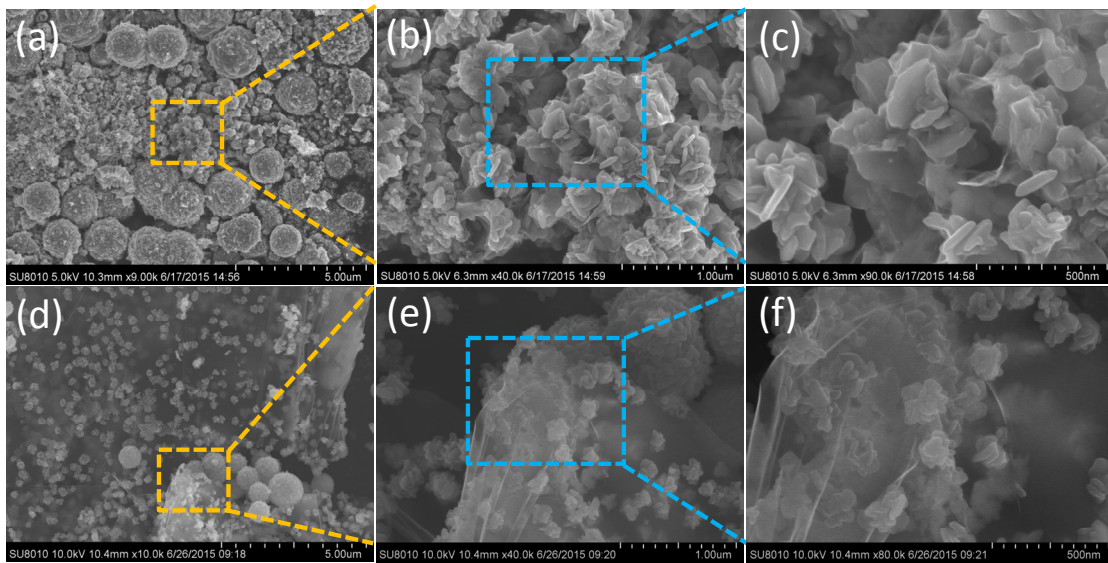


Fig. S6 Low- and high-magnification FESEM images of the prepared reduced graphene oxide and VO₂ hybrids by adding 3 mL of VOCl₂O₄ solution (0.11 M) and 5 mL of GO deionized water dispersion (a-c) or 5 mL of GO butanol dispersion (d-f), followed by solvothermal treatment at 200 °C for 8h.

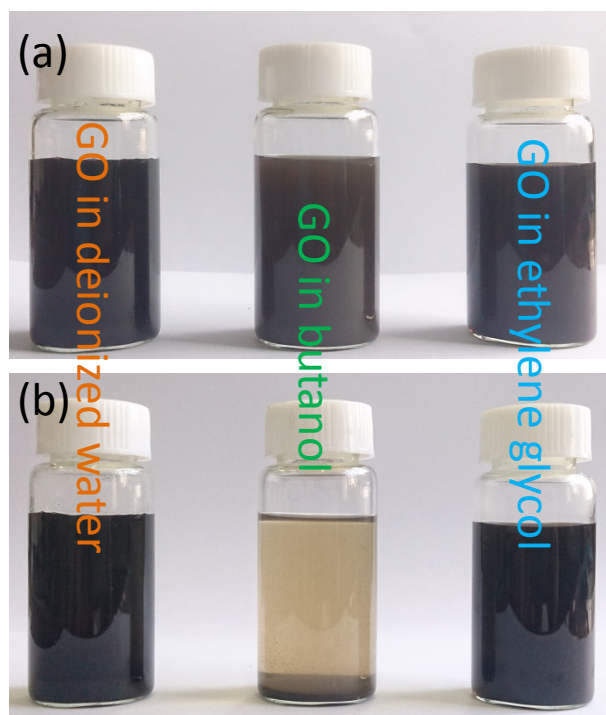


Fig. S7 Digital photographs of graphite oxide dispersion (2 mg mL^{-1}) after relaxing for (a) 0.5 h and (b) 6 h.

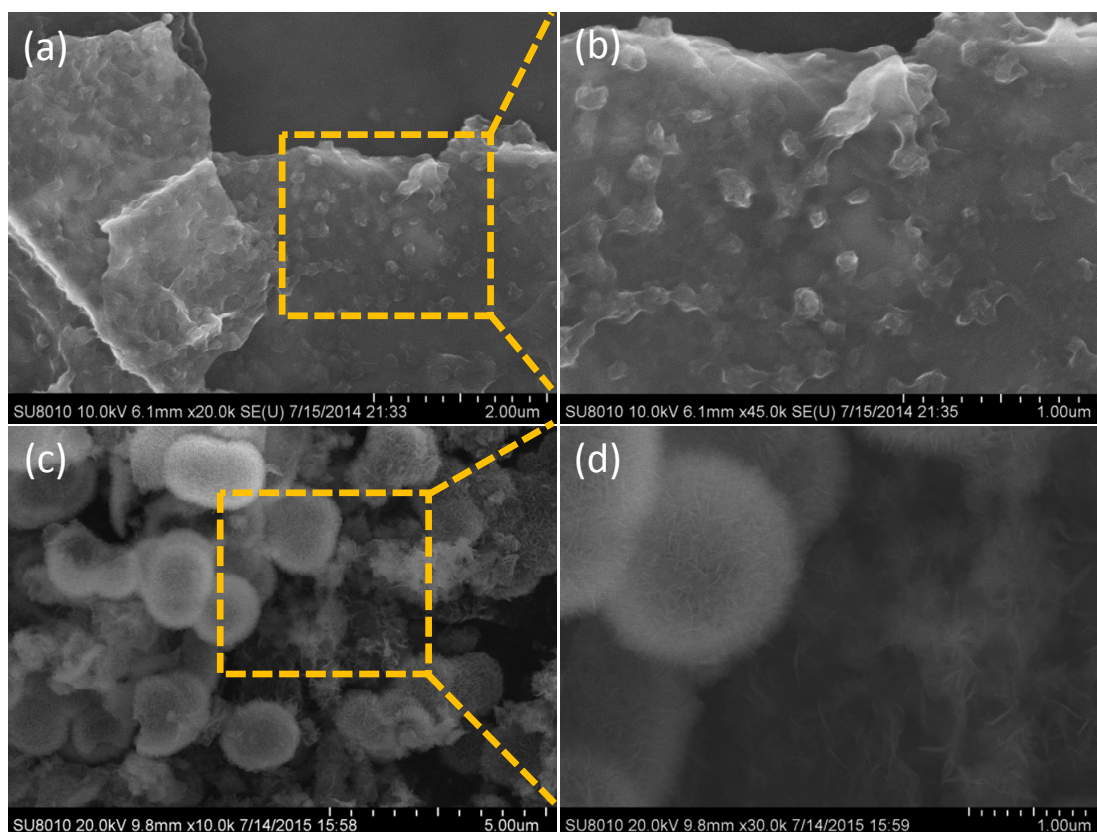


Fig. S8 Low- and high-magnification FESEM images of the reduced graphene oxide and VO₂ hybrids prepared with 3 mL of VOCl₂O₄ solution (0.11 M) and 5 mL of GO ethylene glycol dispersion (2 mg mL⁻¹) at 200 °C reaction for 8h: (a, b) deionized water as reaction solvent and (c, d) ethylene glycol as reaction solvent.

Experimental Section

Preparation of cG-encapsulated M (M = Zn₂SnO₄, SnO₂, and Ni₃S₂/Ni). Hollow Zn₂SnO₄ boxes, porous SnO₂ nanotubes, and Ni₃S₂ nanobundle arrays grown on nickel foam were synthesized according to our previous work.²⁻⁴ Essentially equivalent to the encapsulated procedures of VO₂, viz., 10 mg M powder material and 5 mL of the prepared GO ethylene glycol dispersion (2 mg mL⁻¹) were added into a 50 mL Teflon container pre-filled with 30 mL of isopropanol. After stirring for 30 minutes, the container was sealed in a steel autoclave and kept in an electrical oven at 160 ~ 200 °C for 8 h. After cooling down naturally, the final product was collected by vacuum filtration, alcohol washing, and hot-blast drying of the reaction precipitate.

References

- 1 G. He, L. Li and A. Manthiram, *J. Mater. Chem. A*, 2015, **3**, 14750–14758.
- 2 Y. Zhao, Y. Huang, W. Zhang, Q. Wang, K. Wang, M. Zong and X. Sun, *RSC Adv.*, 2013, **3**, 23489–23494.
- 3 Y. Zhao, X. Li, L. Dong, B. Yan, H. Shan, D. Li and X. Sun, *Int. J. Hydrogen Energy*, 2015, **40**, 14338–14344.
- 4 X. Song, X. Li, Z. Bai, B. Yan, D. Li, X. Sun, *Nano Energy*, 2016, **26**, 533–540.