Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Carambola Shaped VO_2 Nanostructures: A Binder–Free Air Electrode for Aqueous Na–Air Battery

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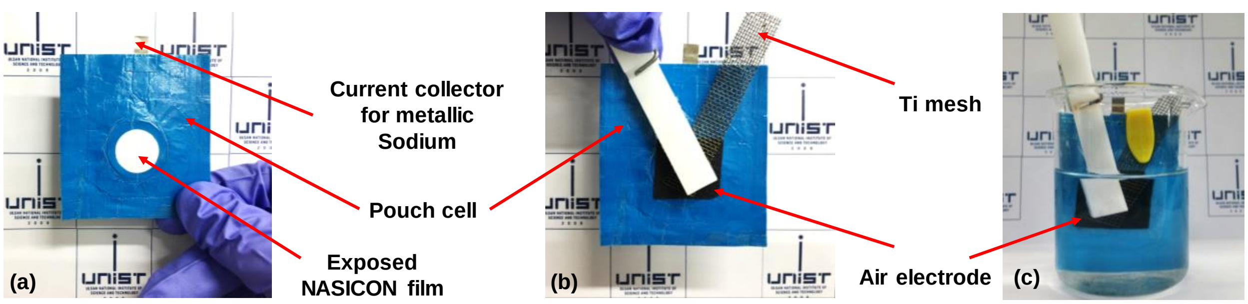
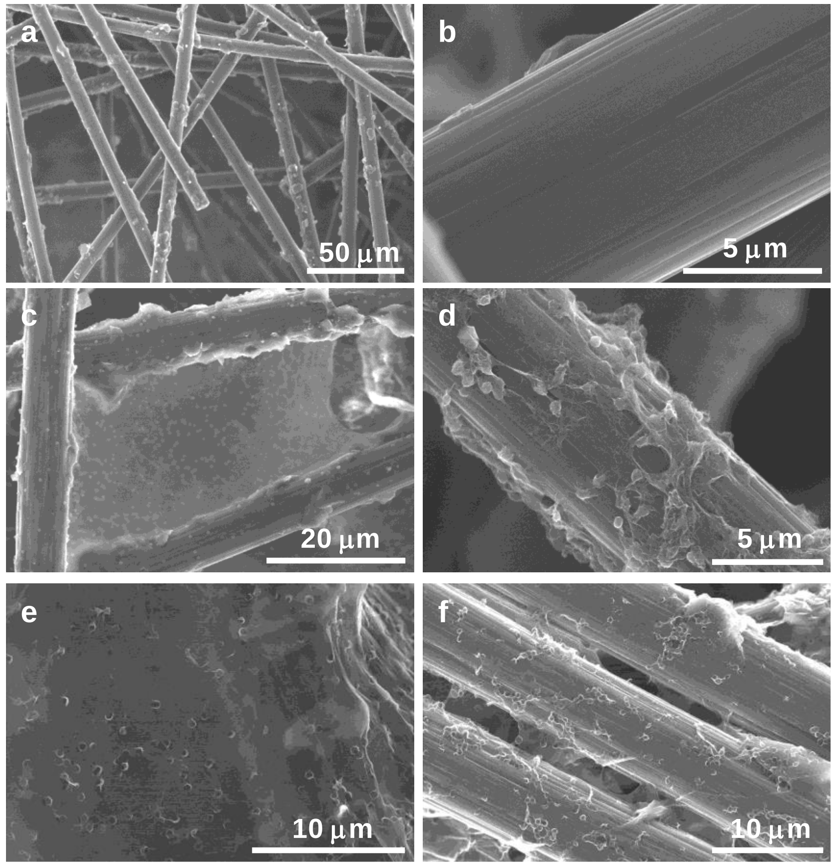
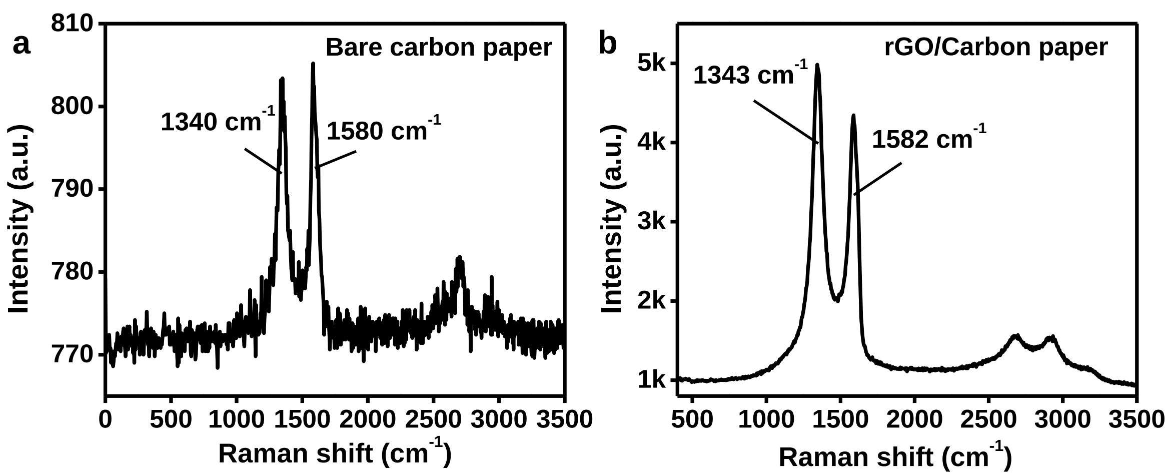
Details of Aqueous Na-air cell fabrication



Supplementary Fig. S1 (a) pouch cell containing sodium anode, organic electrolyte and NASICON; (b) anode pouch cell with air electrode; (c) aqueous Na-air cell.

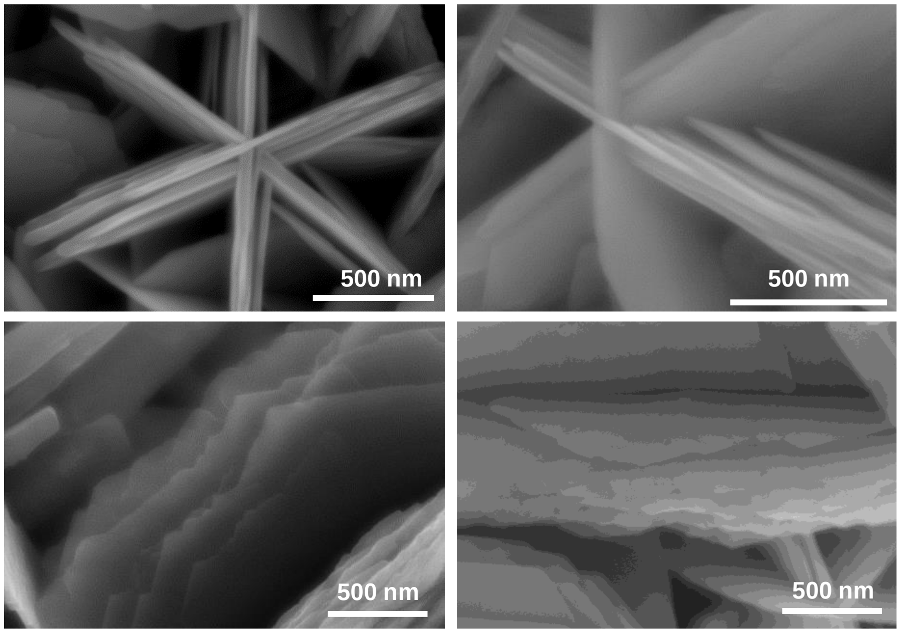


Supplementary Fig. S2 (a) & (b) SEM images of piranha treated carbon paper. SEM images of rGO/carbon paper (c) & (d) with polystyrene and (e) & (f) after etching polystyrene.



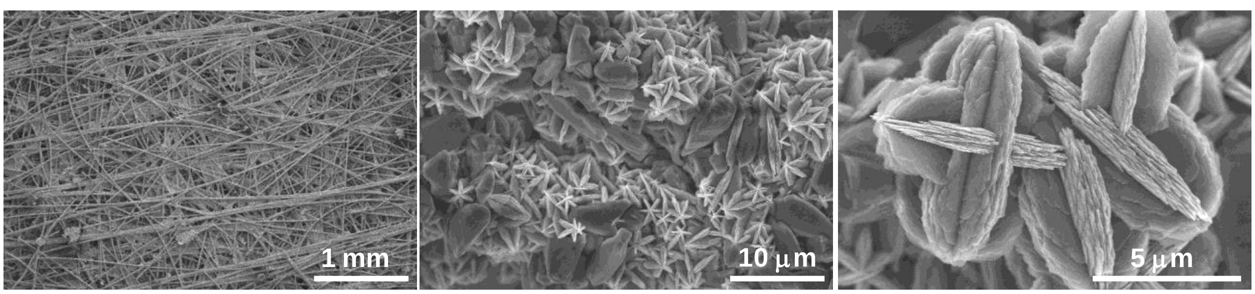
Supplementary Fig. S3 Raman spectra of (a) piranha treated carbon paper (b) rGO coated carbon paper.

High resolution SEM images of VGC electrode

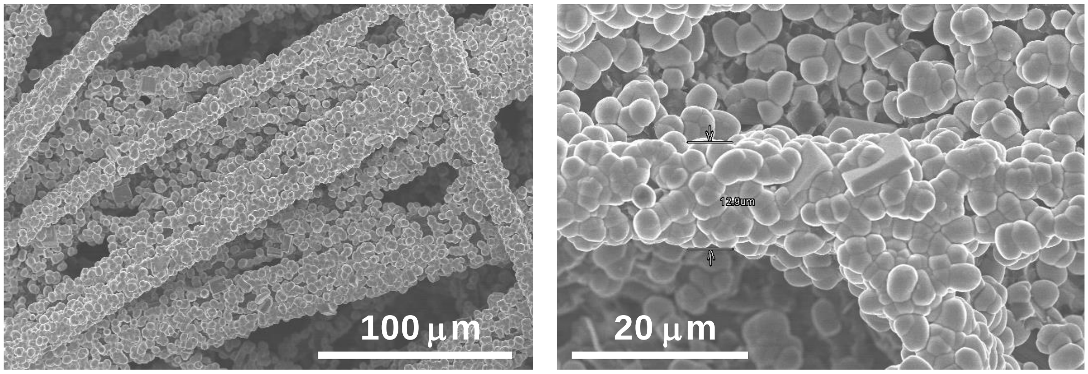


Supplementary Fig. S4 High resolution SEM images of as grown VO_2 on top of rGO coated carbon paper.

SEM image of VGC prepared after 48 h hydrothermal

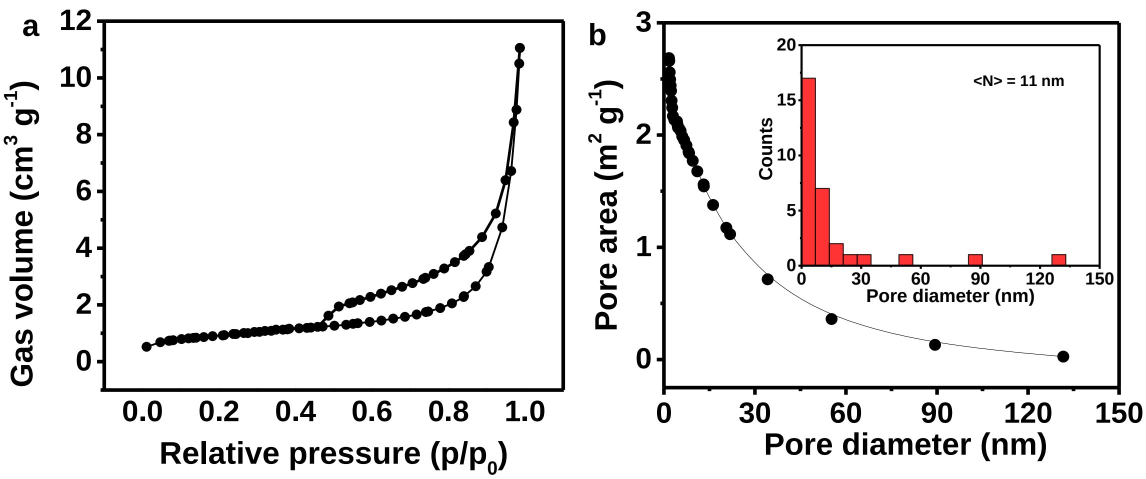


Supplementary Fig. S5 SEM images of VGC electrode at different magnification prepared after 48 h hydrothermal treatment. After 48 h, carambola shaped was observed along with random bulk grain like morphology.

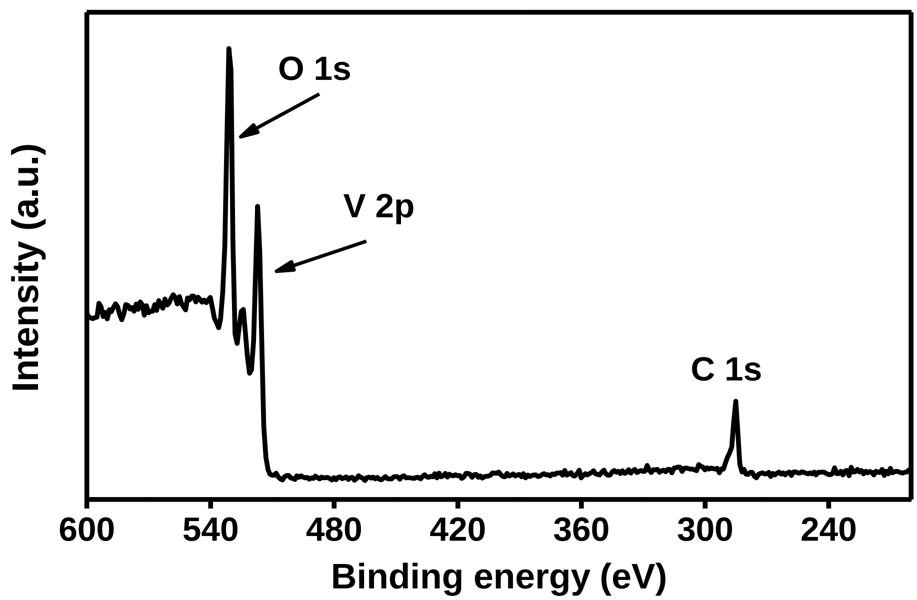


Supplementary Fig. S6 SEM images of VO_2 grown on carbon paper (without rGO coating) after 24 h hydrothermal treatment. Non-uniform coating of VO_2 spherical particles was observed.

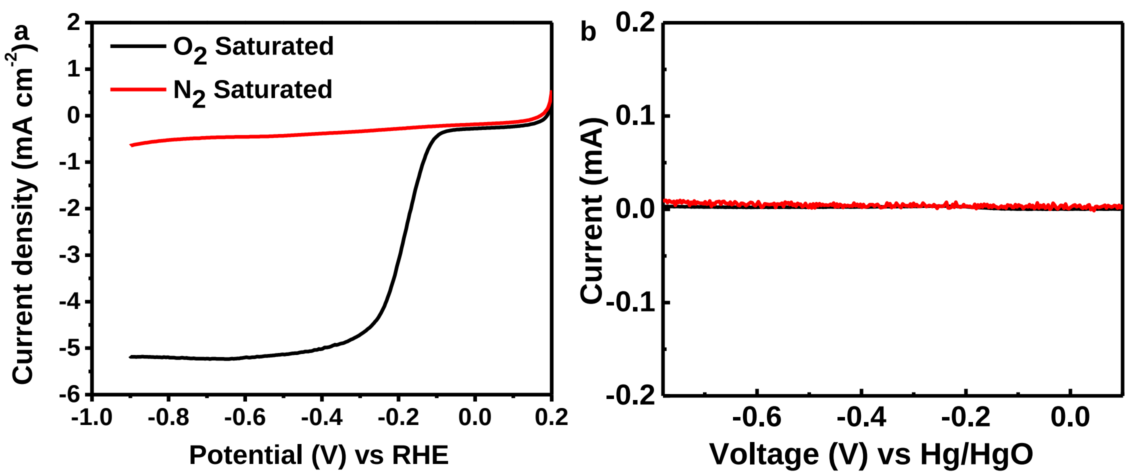
Nitrogen adsorption desorption isotherm plot



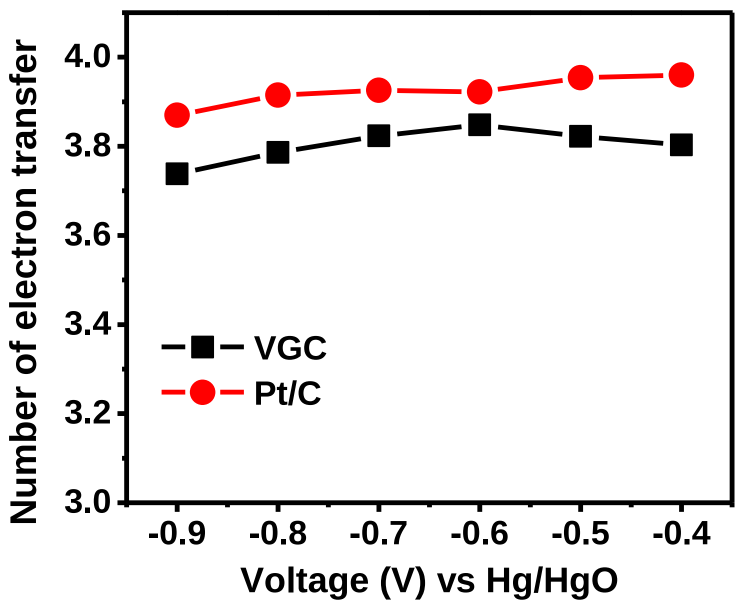
Supplementary Fig. S7 (a) Adsorption/desorption isotherm plot. (b) pore area vs pore diameter plot; the inset shows a histogram for the pore size diameter distribution.



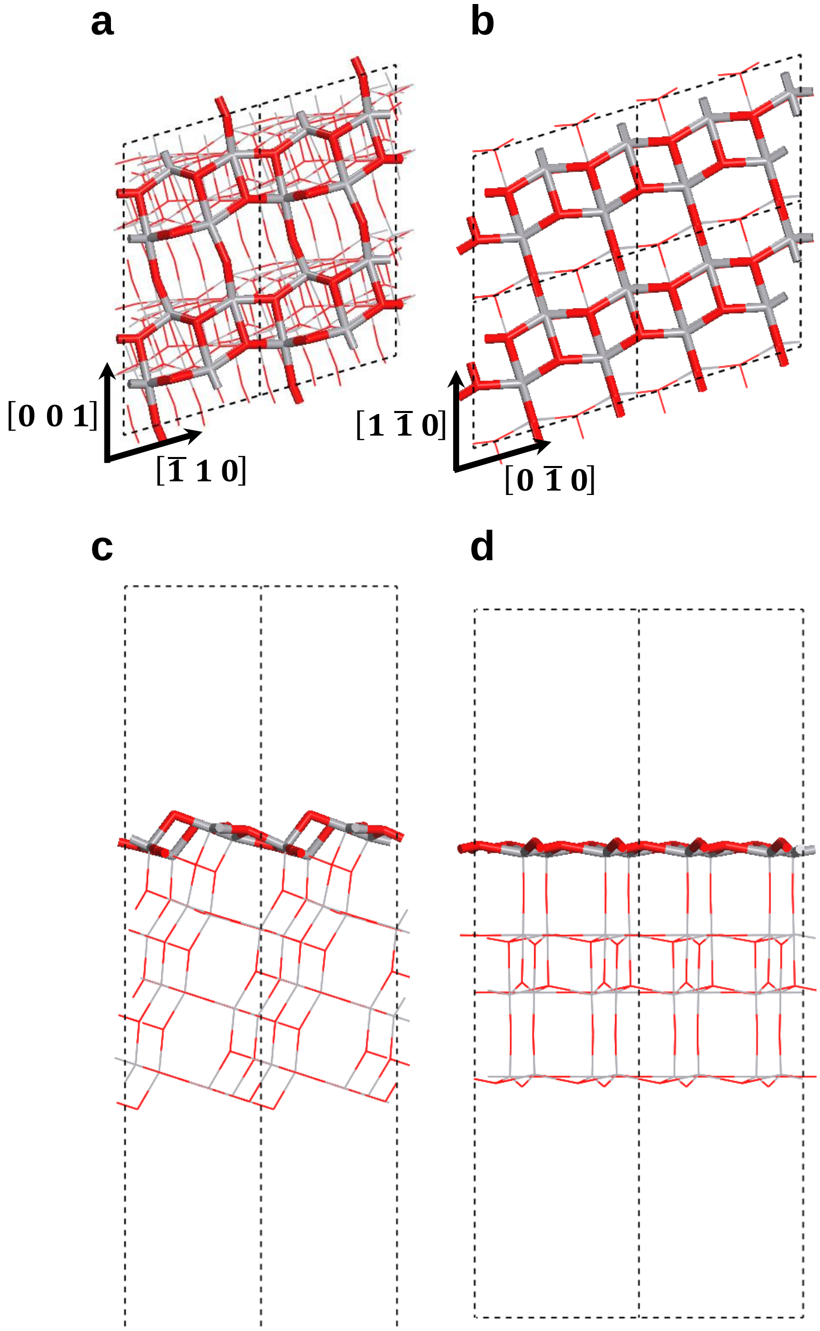
Supplementary Fig. S8 XPS survey spectra for VGC



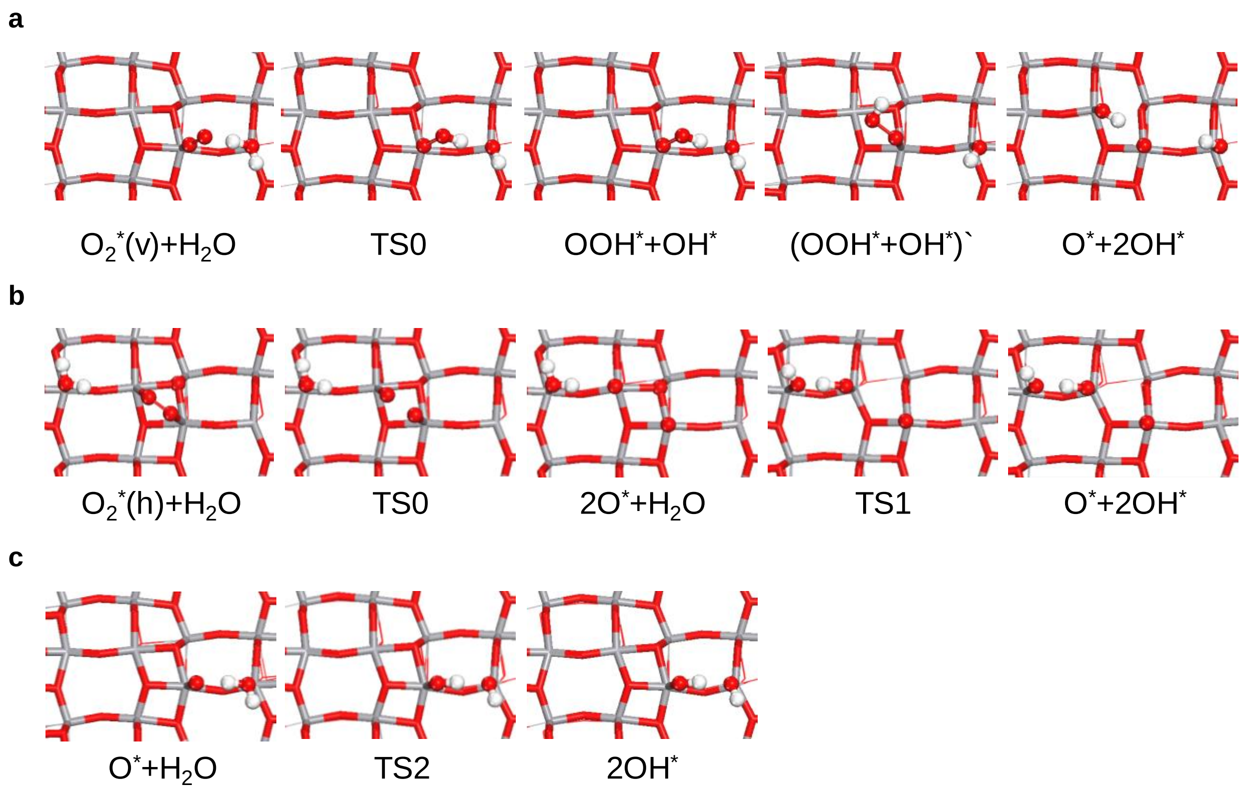
Supplementary Fig. S9 (a) LSV curves associated with ORR of VGC in O_2 and N_2 saturated 0.1 M NaOH solution at 1600 rpm rotating speed with 10 mV s^{-1} scan rate; (b) Polarization curve associated with ORR which shows the ring current at 1600 rpm.



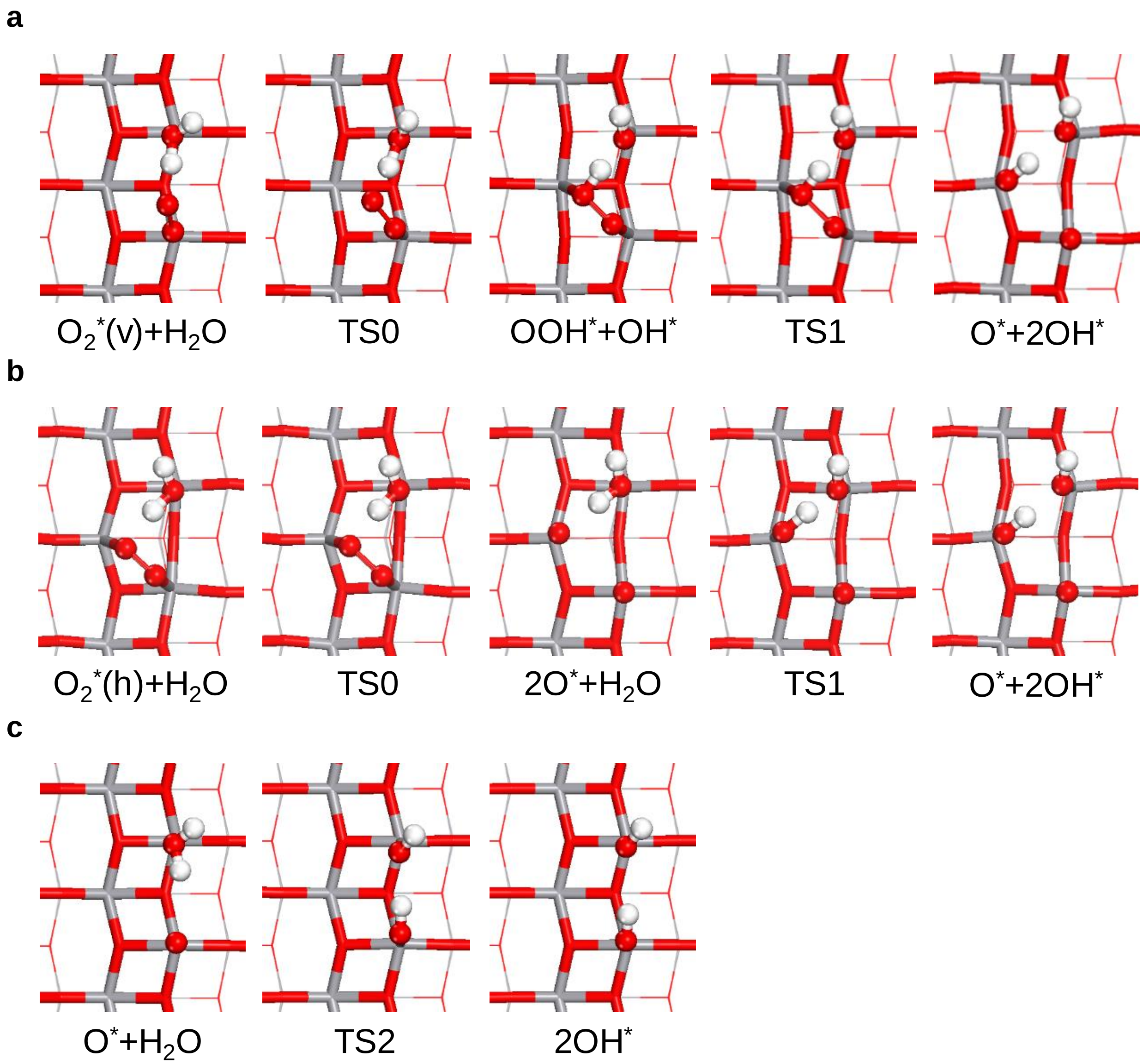
Supplementary Fig. S10 Plot of electron transfer number vs different voltage associated with ORR for oxygen and nitrogen saturated solution of NaOH.



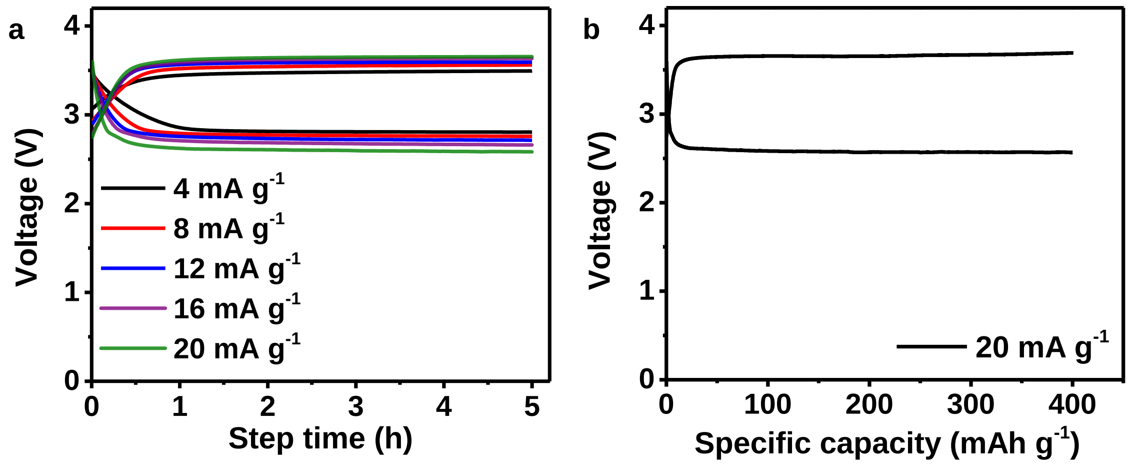
Supplementary Fig. S11 Calculation models for (1 1 0) and (0 0 1) surface of VO_2 (B) phase, respectively. a and c Slab models of (1 1 0) surface of VO_2 b and d (0 0 1) surface of VO_2. a and b represent the top view, and c and d represents side view, respectively. The direction of the basis vector of each surface is represented as arrow with crystallographic direction of the unit cell. V atoms are gray, and O atoms are red.



Supplementary Fig. S12 Reaction mechanisms at VO_2 (1 1 0) surface. a) associative mechanism up to O^*+$2OH^*$ generation. b) dissociative mechanism up to O^*+$2OH^*$ generation. c) O^* + H_2O → $2OH^*$. V atoms are gray, O atoms are red, and H atoms are white.

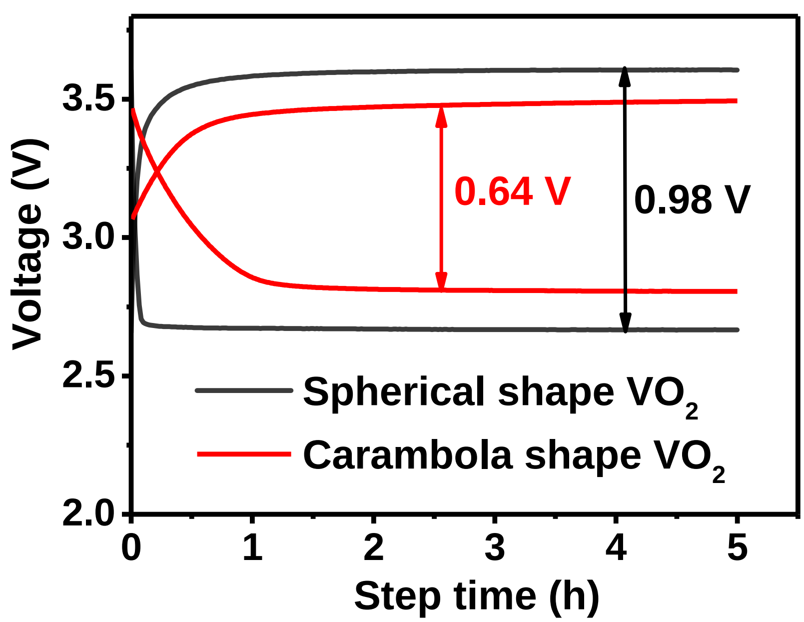


Supplementary Fig. S13 Reaction mechanisms at VO_2 (0 0 1) surface. a) associative mechanism up to O^*+2OH^* generation. b) dissociative mechanism up to O^*+2OH^* generation. c) $O^* + H_2O \rightarrow 2OH^*$. Color scheme is the same as in Figure S12.



Supplementary Fig. S14 (a) Galvanostatic charge-discharge of aqueous Na-air cell at current density ranging from 4 mA g^{-1} to 16 mA g^{-1} (b) 20 h charge-discharge profile at 20 mA g^{-1} current density which shows that aqueous Na-air cell can give 400 mAh g^{-1} specific capacity.

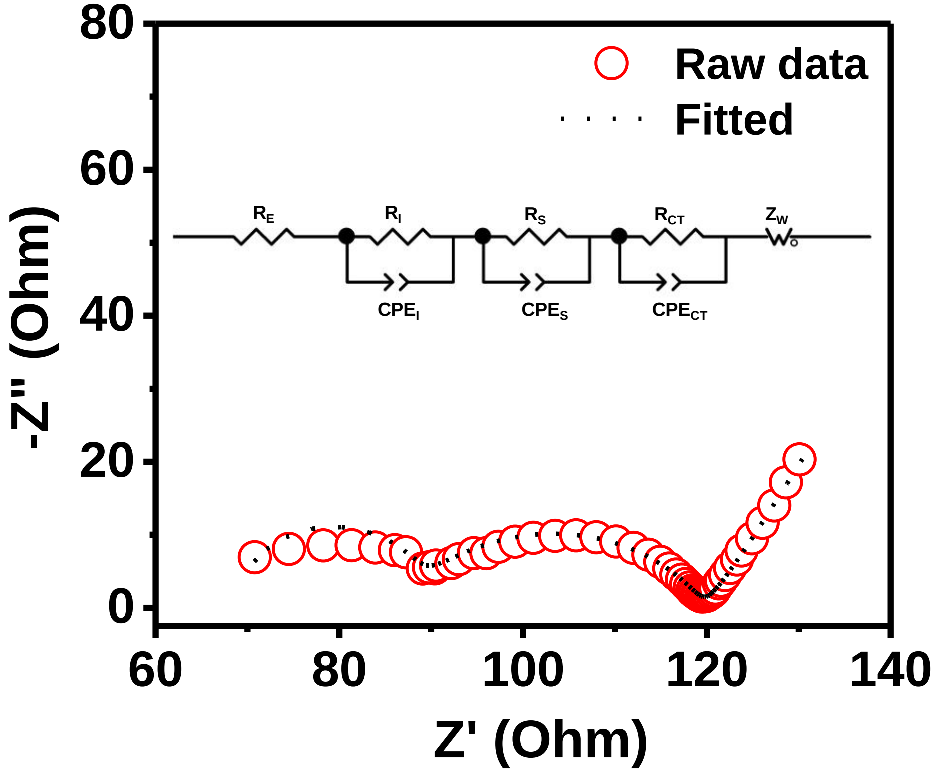
Effect of morphology on cell performance



Supplementary Fig. S15 Comparative charge-discharge profile of carambola and spherical shaped VO_2 at 4 mA g^{-1} (0.01 mA cm^{-2}) current density.

Electrochemical impedance spectroscopy analysis

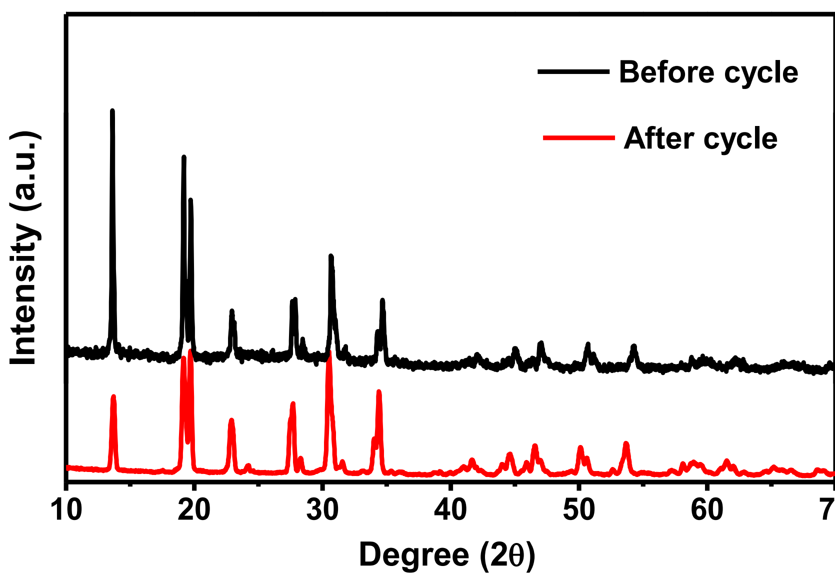
The electrochemical impedance spectroscopy (EIS) technique is a reliable tool for the exploration of different kinds of resistance in the cell. Herein, impedance measurement was carried out for the hybrid Na-air cell at the open circuit voltage having the structure of Na|organic electrolyte|NASICON membrane|NaOH aqueous electrolyte|VGC air electrode. The Nyquist plot of aqueous Na-air cell with air electrode has been shown in Supplementary Figure S16 which displays a typical impedance profile of dual electrolyte system.[1,2] The inset of figure shows an equivalent electric circuit which was used to simulate the spectra.[2,3]



Supplementary Fig. S16 Nyquist plot for the hybrid aqueous Na-air cell with VGC as an air electrode. The inset shows an equivalent circuit which have been utilized to fit the measured data (solid spheres). The dashed line represents the fitted spectra.

R_E is the bulk resistance of the cell which includes the resistance of both liquid electrolytes (organic and aqueous) and the bulk resistance of solid electrolyte membrane. The semicircle in the high frequency region represents all kinds of interfacial resistances (R_I) between the solid and liquid electrolyte and the grain boundary resistance of solid electrolyte membrane.[2] The middle frequency semicircle is attributed to the resistance (R_S) of solid electrolyte interphase (SEI) on the metallic sodium surface, and the charge-transfer resistance (R_{CT}) in an air electrode.[4,5] CPE_I, CPE_S and CPE_{CT} are associated with their relative capacitances originated from constant phase elements. Z_W is the Warburg impedance in low frequency region and is related to a combined effect of diffusion process in air electrode. Based on the fitted equivalent circuit, R_E, R_I, R_S, and R_{CT} values were calculated to be 69.8, 20.9, 25.2, and 22.4 Ω in the open circuit condition, respectively. The Warburg coefficient was calculated to be 15.1 $\Omega\ s^{-1/2}$.

XRD pattern of NASICON solid electrolyte membrane before and after cycles



Supplementary Fig. S17 NASICON X-ray diffractogram before and after electrochemical charge-discharge experiments (50 cycles).

Reference

1. L. Li, X. Zhao and A. Manthiram, *Electrochem. Commun.*, 2012, **14**, 78.
2. F. Liang and K. Hayashi, *J. Electrochem. Soc.*, 2015, **162**, A1215.
3. P. He, Y. Wang and H. Zhou, *J. Power Sources*, 2011, **196**, 5611.
4. X. J. Chen, A. Shellikeri, Q. Wu, J. P. Zheng, M. Hendrickson and E. J. Plichta, *J. Electrochem. Soc.*, 2013, **160**, A1619.
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