Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting information

The intercalation of tetrachlorobenzoquinone mediated by N-methylpyrrolidone into V_2O_5 as cathode for aqueous zinc-ion battery†

Experimental Section

Materials

Vanadium pentoxide (V_2O_5) and N-methylpyrrolidone (NMP) were purchased from Shanghai Aladdin Biochemical Technology Co. Ltd. Tetrachlorop-benzoquinone (TCB) was purchased from Shanghai Bide Pharmaceutical Technology Co. Ltd. Glass fiber membrane (GF/D grade) was provided by Whatman company. Zinc foil (diameter: 15 mm, thickness: 0.3 mm) was purchased from Dongguan Keloude Experimental Materials Technology Co. Ltd. Titanium foil (diameter: 15 mm, thickness: 0.1 mm) was purchased from Guangzhou Haiyuan Metal Products Co. Ltd. Conductive carbon black (Super P Li) was purchased from Guangdong Candlelight New Energy Technology Co. Ltd. Polyvinylidene fluoride (PVDF) was purchased from Wuyu Chemical Industry Co. Ltd. Zinc trifluoromethylsulfonate ($Zn(CF_3SO_3)_2$) was purchased from Shanghai McLean Biochemical Technology Co. Ltd.

Synthesis of s-NMP-V_2O_5 and s-NMP-TCB-V_2O_5

The s-NMP-TCB-V_2O_5 was synthesized by one-step solvothermal method. 0.3 g of V_2O_5 and 0.1 g of TCB were added into solvent that mixed by 15 ml of NMP and 10 ml of deionized water. This suspension was ultrasonic treated for half an hour, then sealed in a 50 mL autoclave and kept at 140 ℃ for 24 hours. The product is collected by centrifugal precipitation and washed by deionized water and dichloromethane for several times, finally dried at 80 ℃ for 12 hours. Following the same conditions, s-NMP-V_2O_5 is prepared without adding TCB.

Characterizations

The crystal structure of the sample was obtained by the radiation X-ray diffractometer (XRD, Japan Science, SmartLab3), and the Fourier infrared spectrum (FTIR) came from the infrared spectrometer (ThermoFisher Nicolet iS-10). Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) mapping images of the samples were obtained by J Hitachi S-4800 instrument equipped with an EDS (AMETEK) analyzer at an accelerated voltage of 3 kV. X-ray photoelectron spectroscopy (XPS) analysis was performed on the Thermo ESCALAB 250 X-ray photoelectron spectrometer. Electron paramagnetic resonance (EPR) spectroscopy was performed using an EPR (BRUKE EMXPLUS) with a central field of 3600 G and a scanning width of 100G. Nitrogen (N_2) adsorption-desorption curves were measured by a 3Flex three-station universal gas adsorbent (Micromeritics, USA). Thermogravimetric (TG) curves were measured from 50 ℃ to 800 ℃ in N_2 atmosphere by TGA/SDTA851E (Mettler Toledo). All cyclic voltammetric tests (CV) were obtained using CHI760E electrochemical workstation (Chenhua, Shanghai, China). The constant current charge/discharge (GCD) test with voltage range of 0.1V to 1.6 V was conducted on LAND CT2001A (5 V/5 mA).

Battery fabrication

Samples (V_2O_5 or s-NMP-V_2O_5 or s-NMP-TCB-V_2O_5) are mixed with Super P Li and PVDF at the ratio of 6:3:1, then NMP is added and fully milled, the resulting slurry is coated on titanium foil, and dried in vacuum at 80 ℃ for 12 hours. The average mass loading is kept in the range of 1.3-1.7 mg cm^{-2}. The CR2032 button battery is used, and the assembly process is in air atmosphere (Zinc foil as anode; glass fiber as separator), with 3 M $Zn(CF_3SO_3)_2$ as aqueous electrolyte. All fabricated batteries were stood at room temperature for 12 hours before the electrochemical test.

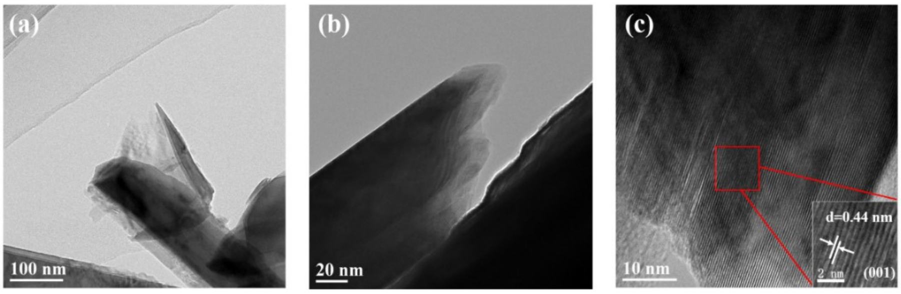

Fig. S1 HRTEM image of the interplanar spacing for the V_2O_5 corresponding.

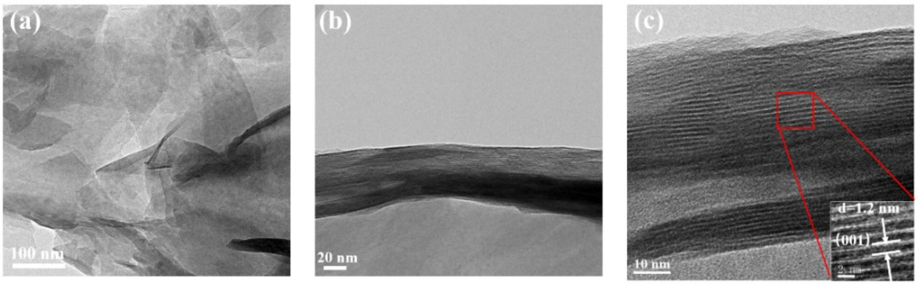

Fig. S2 HRTEM image of the interplanar spacing for the s-NMP-V_2O_5 corresponding.

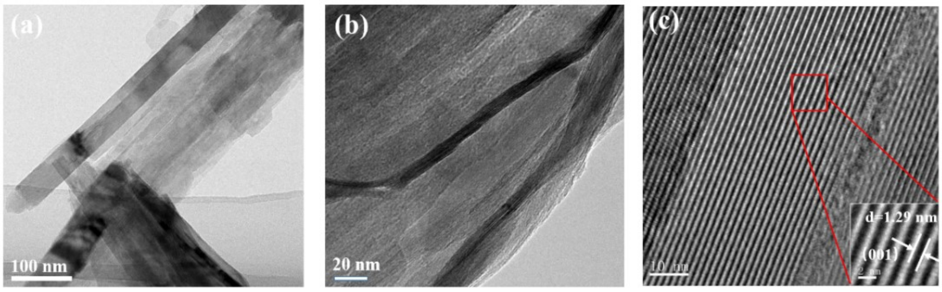

Fig. S3 HRTEM image of the interplanar spacing for the s-NMP-TCB-V_2O_5 corresponding.

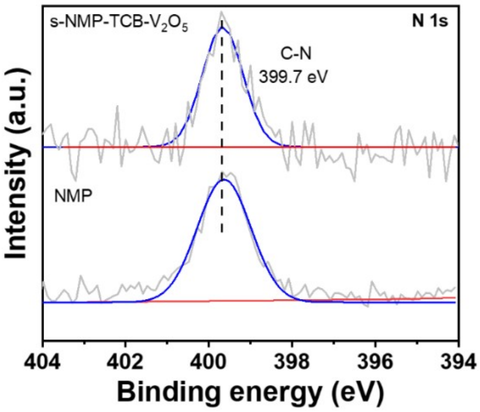

Fig. S4 N 1s regions of high-resolution XPS spectra for NMP and s-NMP-TCB-V_2O_5.

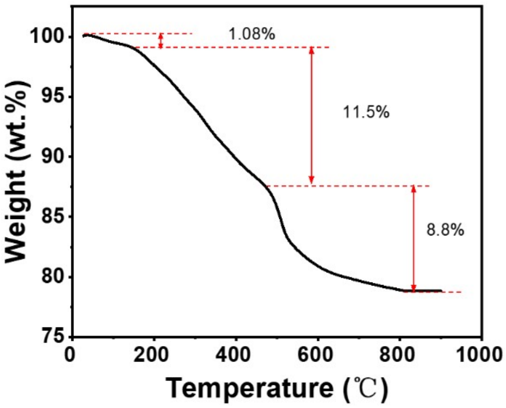

Fig. S5 TG curves of s-NMP-TCB-V_2O_5.

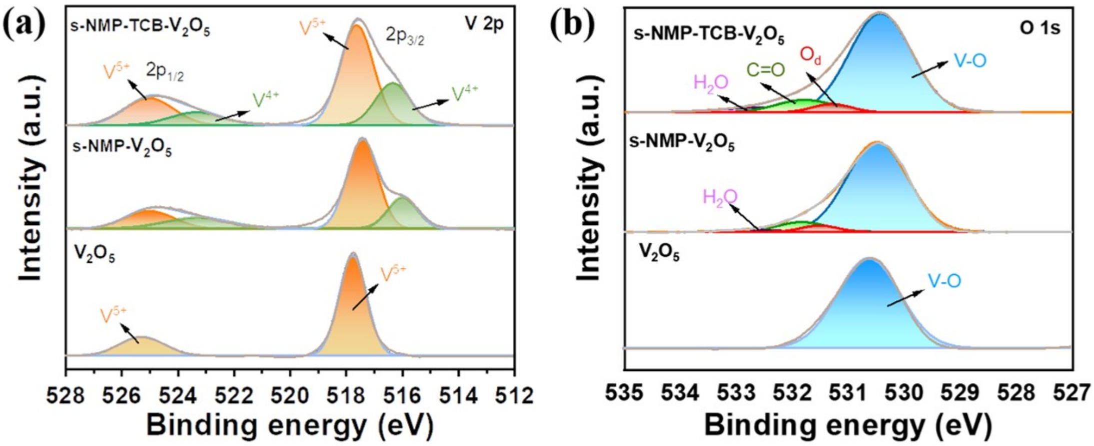

Fig. S6 High-resolution XPS spectra of (a) V 2p and (b) O 1s for V_2O_5, s-NMP-V_2O_5 and s-NMP-TCB-V_2O_5.

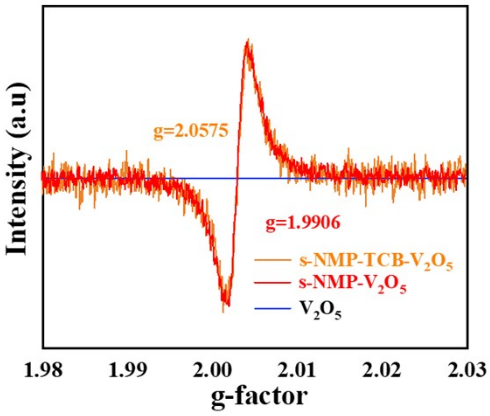

Fig. S7 EFP spectrum of V_2O_5, s-NMP-V_2O_5 and s-NMP-TCB-V_2O_5.

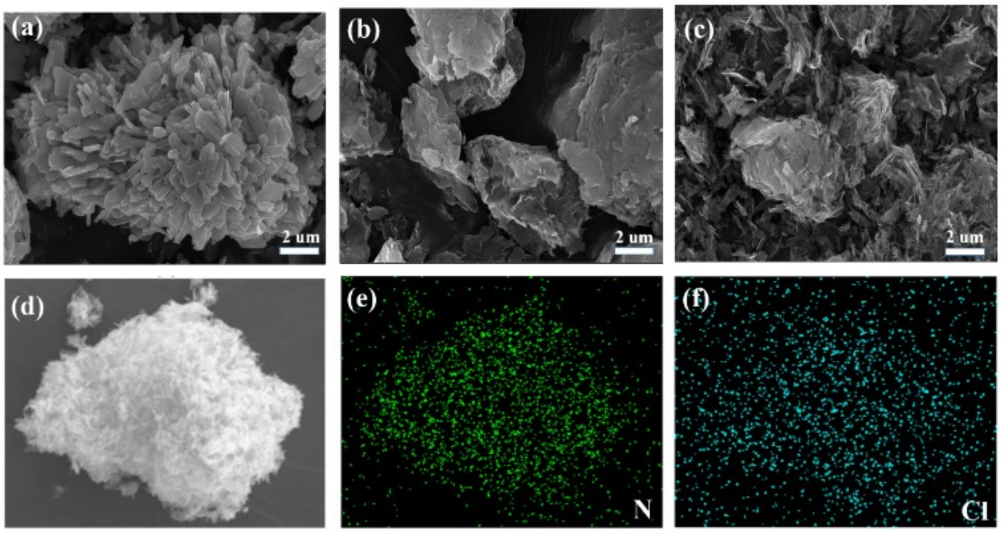

Fig. S8 SEM images of (a) commercial V_2O_5, (b) s-NMP-V_2O_5 and (c) s-NMP-TCB-V_2O_5; (d) SEM-EDS elemental mapping of s-NMP-TCB-V_2O_5 on (e) N and (f) Cl elements.

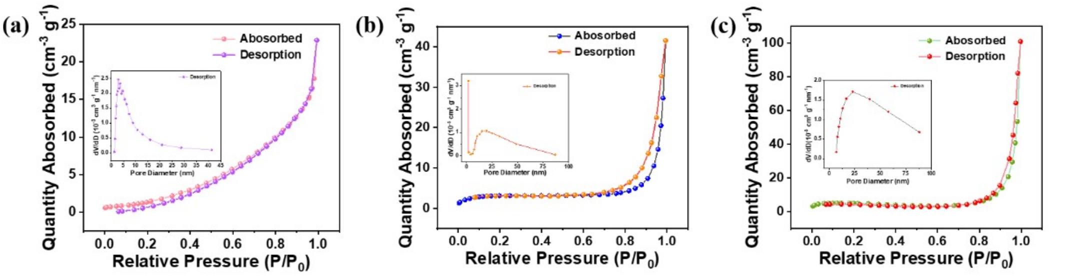

Fig. S9 N_2 physisorption isotherms and pore size distribution (inset) of (a) commercial V_2O_5, (b) s-NMP-V_2O_5 and (c) s-NMP-TCB-V_2O_5.

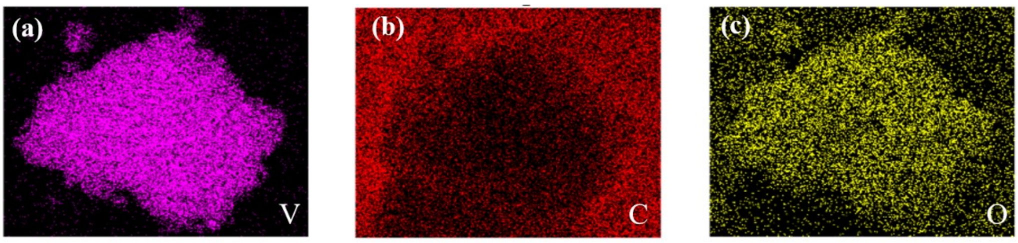

Fig. S10 SEM-EDS mapping images of s-NMP-TCB-V_2O_5 for (a) V, (b) C and (c) O elements.

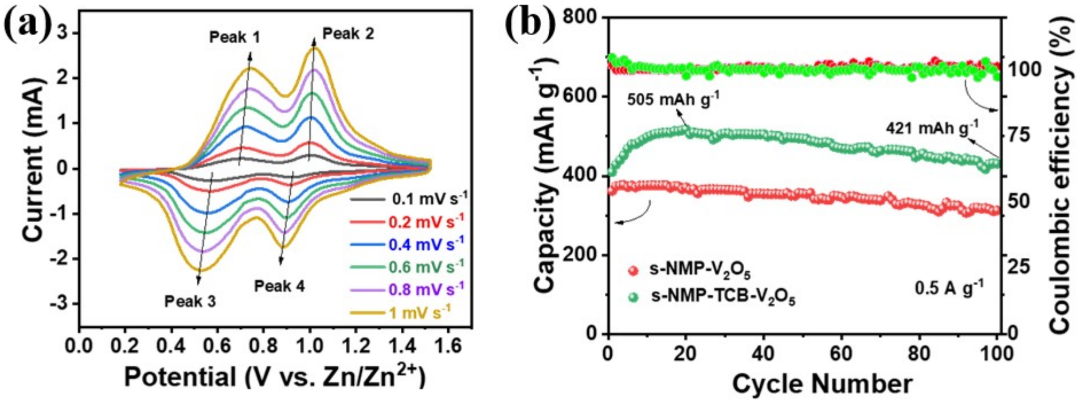

Fig. S11 (a) CV curves of s-NMP-TCB-V_2O_5 at various sweep rates; (b) cycle performance comparison of s-NMP-TCB-V_2O_5 and s-TCB-V_2O_5 at 0.5 A g^{-1}.

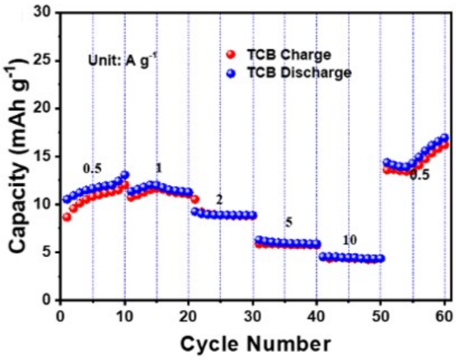

Fig. S12 Rate performance of TCB at different current densities.

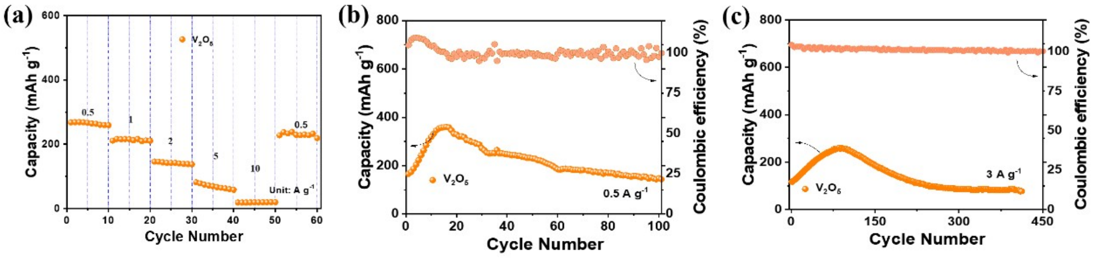

Fig. S13 (a) Rate performance of V_2O_5 at different current densities. (b) Constant current charge and discharge test of V_2O_5 at 0.5A g^{-1} current density. (c) Long-cycle test of V_2O_5 at 3A g^{-1} current density.

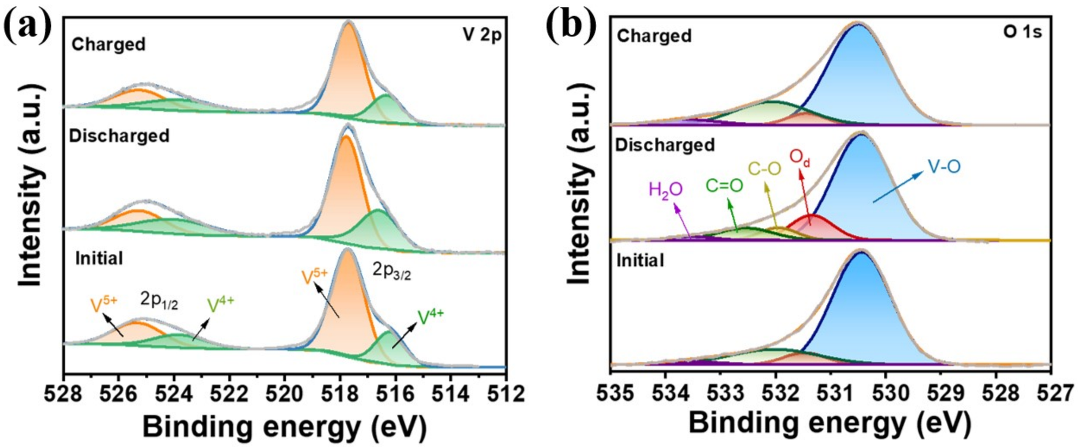

Fig. S14 XPS analysis of s-NMP-TCB-V_2O_5 at initial, discharge (0.1 V) and charge state (1.3 V) in ZIBs for (a) V 2p and (b) O 1s.

Table. S1 Comparison of electrochemical performance of new organic-inorganic combined cathode materials for rechargeable zinc batteries corresponding to Fig. 2e.

Material	**Electrolyte**	**Voltage Range**	**Capacity (Current density)**	**Capacity retention @current density (Cycle number)**	**Reference**
(1, 2, 3-BQ)-VO	3 M $Zn(CF_3SO_3)_2$	0.1-1.6 V	446 mA h g^{-1} (0.2 A g^{-1})	85.4%@5 A g^{-1}（1800 cycles）	S1
MgVOH /PANI	3 M $Zn(CF_3SO_3)_2$	0.2-1.6 V	412 mA h g^{-1} (0.1 A g^{-1})	88%@4 A g^{-1}（1000 cycles）	S2

VOH-PPy (PSA)	3 M $Zn(CF_3SO_3)_2$	0.2-1.5 V	422 mA h g^{-1} (0.1 A g^{-1})	53.9%@10 A g^{-1}（5000 cycles）	S3
PEDOT/V_2O_5	3 M $Zn(CF_3SO_3)_2$	0.2-1.6 V	247 mA h g^{-1} (0.2 A g^{-1})	88%@10 A g^{-1}（700 cycles）	S4
PAVO	3 M $Zn(CF_3SO_3)_2$	0.2-1.6 V	350 mA h g^{-1} (0.1 A g^{-1})	90%@1 A g^{-1}（900 cycles）	S5
PANI100-V_2O_5	3 M $Zn(CF_3SO_3)_2$	0.4-1.4V	348 mA h g^{-1} (0.5 A g^{-1})	90%@5 A g^{-1}（2000 cycles）	S6
V_2O_5-DETA	3 M $Zn(CF_3SO_3)_2$	0.1–1.5 V	180 mA h g^{-1} (0.5 A g^{-1})	92.1%@4 A g^{-1}（1400 cycles）	S7
s-NMP-TCB-V_2O_5	3 M $Zn(CF_3SO_3)_2$	0.1–1.6 V	452 mA h g^{-1} (0.5 A g^{-1})	85.6%@3 A g^{-1}（1500 cycles）	This work

References:

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