Alumina modified sodium vanadate cathode for aqueous zinc-ion batteries

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Supporting Information

Experimental section

Preparation of NVO

First, 100 mL of NaCl (2.0 mol/L) aqueous solution obtained from China National Pharmaceutical Group Chemical Reagent Co., Ltd. was configured. At room temperature (25 °C), 3.0 g of commercial V_2O_5 powder obtained from China National Pharmaceutical Group Chemical Reagent Co., Ltd. was added to the above NaCl aqueous solution and mixed for 30 minutes under ultrasonic treatment. Then the solution was stirred on a magnetic stirrer for 72 hours, and the solution turned to orange. Afterwards, the solution was centrifuged to obtain the product, and the excess NaCl was washed away by ultra-pure water and alcohol for several times. Finally, the product was dried at 60 °C for 12 hours to obtain sodium vanadate (NVO).

Preparation of NVO@Al_2O_3

Preparation of ammonium formate/formic acid dispersion: First, 0.6306 g of ammonium formate obtained from Aladdin was dissolved in 50 mL of deionized water to obtain 2 M of ammonium formate solution. Then, a dropper was used to take a certain amount of formic acid (Aladdin) to add dropwise to the above solution until a solution with a pH of 4.4 is obtained. Here, the ammonium formate/formic acid achieve a slow heterogeneous growth of Al_2O_3, which provides a suitable environment for manipulating the growth of core-shell structure Al_2O_3 within a precision of nanometer.

Preparation of NVO@Al_2O_3 material: First, 0.2 g of sodium vanadate NVO was dispersed in 50 mL of ammonium formate/formic acid dispersion (pH= 4.4, 0.2 M), and treated with ultrasonic wave for 30 minutes. Then, 0.015 g of aluminum sulfate was added and reacted for 15 minutes in an oil bath at 70 °C with stirring. Finally, the solution was pumped and filtered to obtain the product. The final products were washed by distilled water and ethanol several times and dried in an oven at 70 °C for 12 hours to obtain pure phase NVO@Al_2O_3.

Characterization

X-ray diffraction (XRD) patterns of NVO and NVO@Al_2O_3 were collected on an X-ray diffractometer (model Rigaku Smart Lab TM) at a scan range of 10°–80°. The microstructure and energy dispersive X-ray spectroscopy (EDS) of NVO and NVO@Al_2O_3 were characterized using SEM (Hitachi S4800) and TEM (JEOL, JEM, 2100F). ICP-OES (PerkinElmer 8300) was used to analyze the elemental composition of NVO and NVO@Al_2O_3. The valence state changes of V in NVO@ Al_2O_3 in different charging and discharging states were analyzed using X-ray photoelectron spectroscopy (Thermo, ESCALAB, 250XI).

Electrochemical measurements

The positive electrodes were prepared by mixing active materials, carbon black, and poly(tetrafluoroethylene) (PTFE) with a weight ratio of 7:2:1. The homogeneous slurries with a mass loading of 8 mg/cm^2 were cast onto stainless steel mesh and dried at 60 ℃ for 12 hours. The performance test of the materials was conducted using a 2032-coin cell, with zinc foil as the negative electrode, Whatman glass fibre as the separator, and 2 M $ZnSO_4$ (aq) as the electrolyte. For electrochemical performance testing, the operating voltage range of the full battery is set to 0.3–1.4 V. Cyclic voltammetry (CV) and the electrochemical impedance measurements (EIS) were performed using the CHI 660C electrochemical work station. The EIS data was recorded from 105 to 0.01 Hz with an amplitude of 10 mV. All electrochemical tests were performed at room temperature.

Supplementary Figures

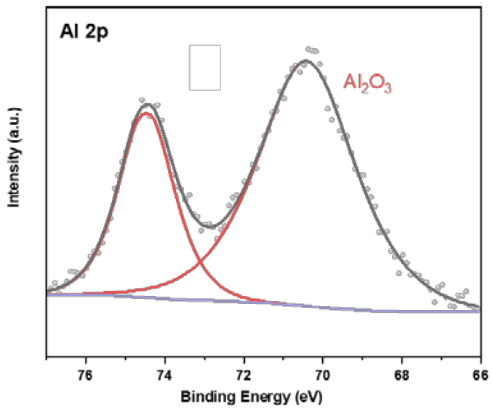

Fig. S1 Al 2p XPS spectra of NVO@Al$_2$O$_3$.

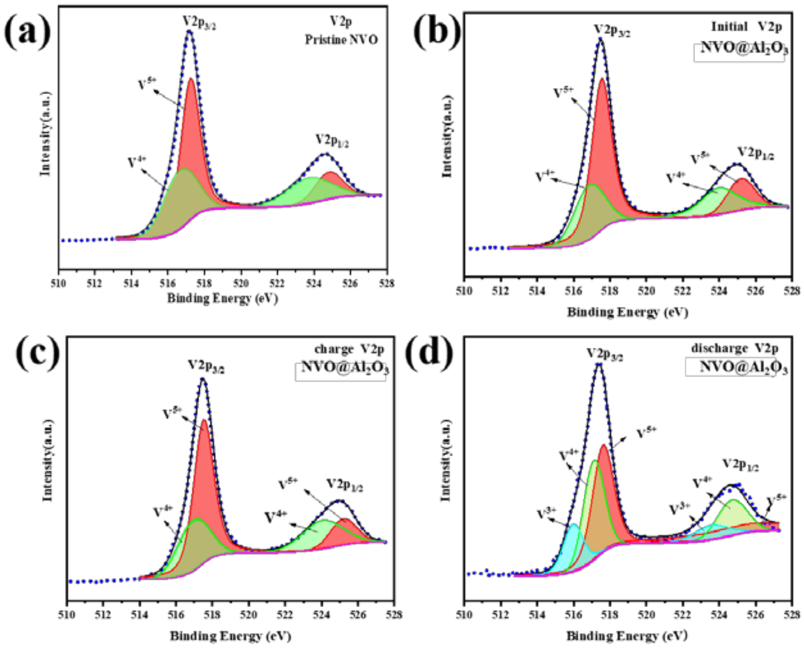

Fig. S2 High-resolution XPS spectra in V 2p.

(a) Pristine NVO; (b) pristine NVO@ Al$_2$O$_3$. (c) NVO@ Al$_2$O$_3$ in charge state; (d) NVO@ Al$_2$O$_3$ in discharge state.

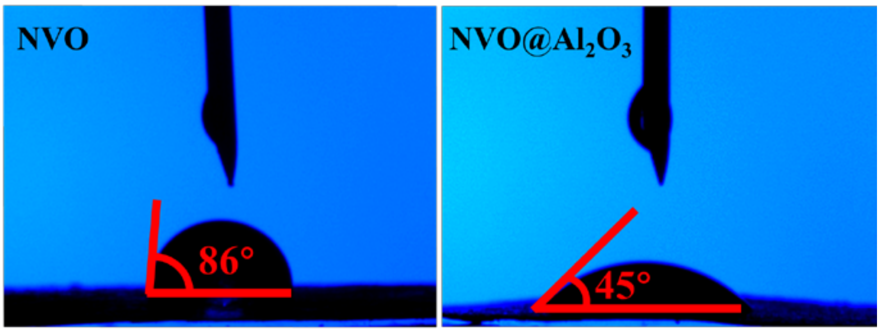

Fig. S3 Wettability of NVO and $NVO@Al_2O_3$ electrode.

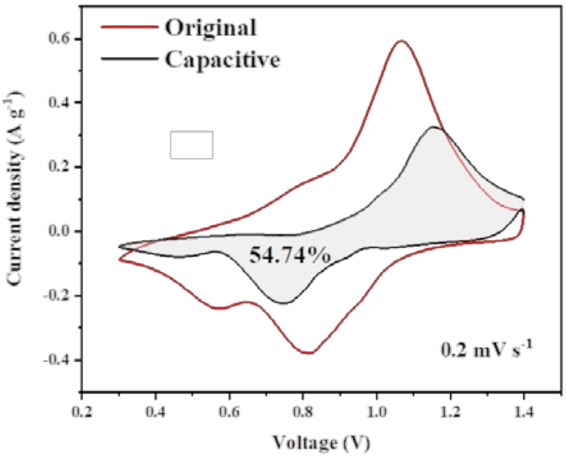

Fig. S4 Surface-controlled capacity contribution ratio (labeled capacitive) in $NVO@Al_2O_3$ battery, obtained at a scan rate of 0.2 mV/s.

Table S1. Performance of ZIBs based on NVO@Al_2O_3 and other Vanadium based cathode materials

Material	Current density	Discharge capacity	Refs.
$NaV_3O_8 \cdot 1.5H_2O$	0.1 A g^{-1}	275 mA h g^{-1}	[1]
	4 A g^{-1}	165 mA h g^{-1}	
Vo$^{\cdot\cdot}$-PNVO	0.1 A g^{-1}	256 mA h g^{-1}	[2]
	4 A g^{-1}	171 mA h g^{-1}	
NaCaVO	0.1 A g^{-1}	347 mA h g^{-1}	[3]
	5 A g^{-1}	154 mA h g^{-1}	
PEDOT-NVO	0.1 A g^{-1}	350 mA h g^{-1}	[4]
	5 A g^{-1}	210 mA h g^{-1}	
3D-NVO	0.1 A g^{-1}	330 mA h g^{-1}	[5]
	4 A g^{-1}	\	
NVO@Al_2O_3	0.1 A g^{-1}	420 mA h g^{-1}	This work
	4 A g^{-1}	250 mA h g^{-1}	

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