Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Engineering the NASICON electrolyte/Na anode interface by amorphous bismuth oxide for sodium battery

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NASICON pellets preparation

The $Na_3Zr_2Si_2PO_{12}$ (NZSP) electrolyte was fabricated by the solid-state reactive sintering method as in our previous study [1]. Briefly, stoichiometric amount of Na_3PO_4 (99%, Energy, China), ZrO_2 (99.99%, 50 nm, Macklin, China) and SiO_2 (99.8%, 7-40 nm, Macklin, China) were mixed by ball-milling at 200 rpm for 10 h in alcohol and then dried at 110 °C overnight. The dried powders were pressed into pellets, followed by being buried with the mother powders and sintered at 950 °C for 10 h with a heating rate of 4 °C min^{-1} under air atmosphere.

BiO_x artificial layer fabrication

Fig. S1 showed the schematic of BiO_x coating on the NZSP pellet. The bismuth(III) 2-ethylhexanoate (92% in 2-ethylhexanoic acid, Shanghai Macklin Biochemical Co., Ltd.) was dissolved in n-hexane (AR, Tianjin Yuanli Co., Ltd.). Then, the precursor was ultrasonicated for 30 min. Subsequently, 15 μL precursor solution was dripped onto the surface of the NZSP pellet each time. To control the loading, 30, 60, 90 μL precursors were loaded on the NZSP electrolyte, which corresponds to 27, 53 and 80 μL cm^{-2}, respectively. Finally, the coated NZSP pellets were irradiated with ultraviolet light (wavelength:185 and 254 nm) at RT for 12 h to form BiO_x. The manufacturer and model name of UV source is Star Creation UV and KSD10165, respectively.

Characterization

The phase structures of the pristine and BiO_x-modified NZSP samples were analyzed by X-ray diffraction (XRD, D/Max-2500, Rigaku) with Cu K_α radiation from 5° to 70°. Fourier transform infrared (FTIR) spectroscopy (Nicolet 6700, Thermo Scientific) was used to monitor the decomposition the Bi precursor. The surface and cross-section microstructures and elemental composition of electrolyte were investigated by field emission scanning electron microscope (FESEM, Apreo S LoVac, FEI) equipped with an energy dispersive spectrometer (EDS) unit. X-ray photoelectron spectroscopy (XPS, Escalab 250Xi, Thermo Fisher Scientific) was recorded to examine the chemical state of BiO_x and Na before and after reaction with Na. The binding energy was calibrated with reference to C 1s at 284.8 eV for the charging effect.

Electrochemical test

The ion conductivity of NZSP was measured by AC impedance spectra on the Ag/NZSP/Ag symmetrical 2032 coin cell on an electrochemical workstation (CHI 760E, Shanghai Chenhua Instruments Co., Ltd.) within 10^6-1 Hz range and with an perturbation amplitude of 5 mV. Prior to test, the Ag slurry was sprayed on both sides of the polished NZSP pellets and heat-treated at 400 ºC for 10 min to eliminate the organics. The ZSimpWin software was used to fit the impedance spectra. The charge/discharge cycling of Na/NZSP/Na symmetric cell and $Na_3V_2(PO_4)_3$ (LE) /NZSP/Na full battery were performed on a LAND CT3002A cell test system (LAND, China) at 30 ºC. For the full battery, the cathode slurry was prepared by mixing $Na_3V_2(PO_4)_3$ (NVP) (Shenzhen Kejing Zhida Technology Co. Ltd), Super P and polyvinylidene fluoride (PVDF) successively with a weight ratio of 8:1:1 in a certain amount of N-methyl-2pyrrolidone (NMP). The resultant slurry was coated on the Al foil and dried in a vacuum oven at 120 °C for 12 h. The loading of NVP is 1.1~1.3 mg cm^{-2}. 5 μL liquid electrolyte (1 M $NaClO_4$ in EC:DMC (1:1) + 5% FEC) was added to decrease the interface impedance between cathode and NZSP electrolyte. The sodium metal electrode was flushed out with a punch and pressed onto the surface of the NZSP by hand as anode. The battery was cycled in the range of 2.5-3.8 V under different current densities at 30 °C.

Supplementary figures

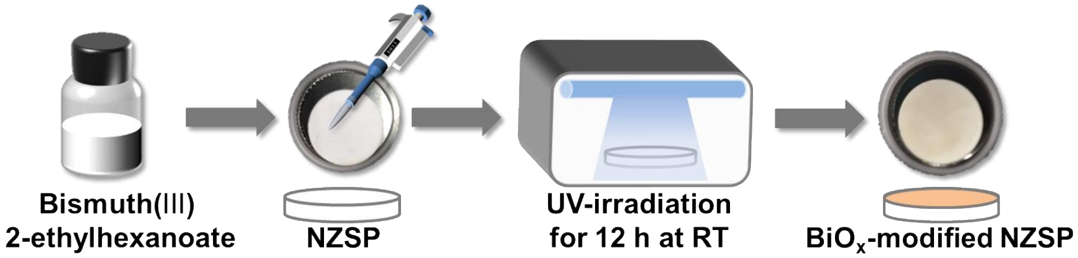

Fig. S1 Schematic illustration of fabricating BiO$_x$ artificial layer on the NZSP pellet.

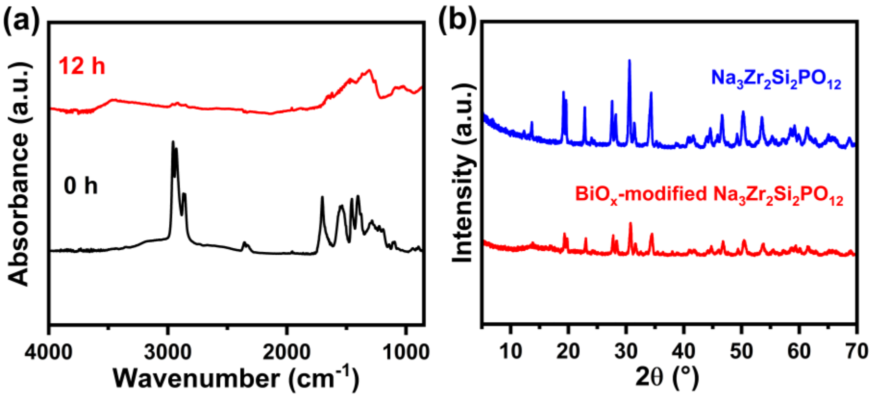

Fig. S2 (a) FTIR spectra of BiO$_x$ layer before and after 12 h of UV-light irradiation. (b) XRD patterns of pristine and BiO$_x$-modified NZSP.

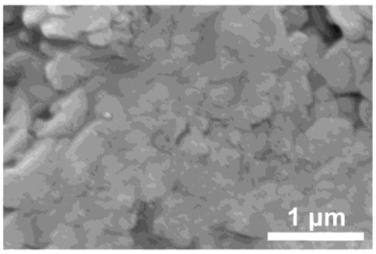

Fig. S3 Surface SEM of pristine NZSP electrolyte.

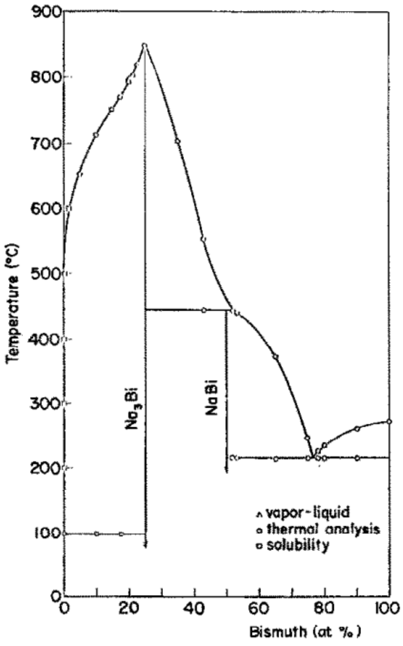

Fig. S4 Phase diagram of Na-Bi system.

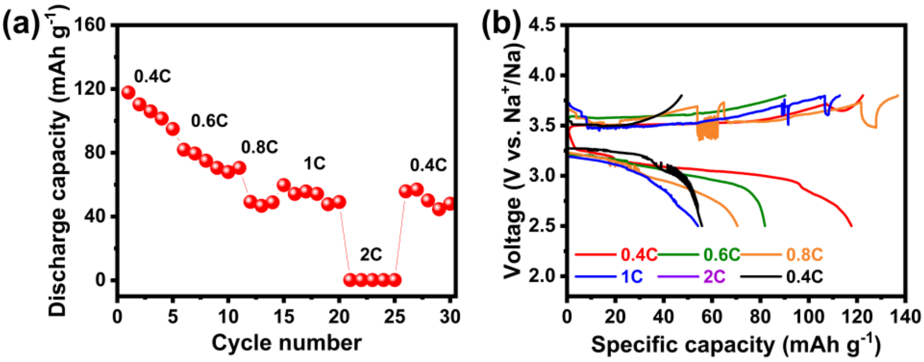

Fig. S5 (a) Rate performance and (b) specified charge/discharge profiles of the $Na_3V_2(PO_4)_3$ (LE)/NZSP /Na full battery at 30 ºC.

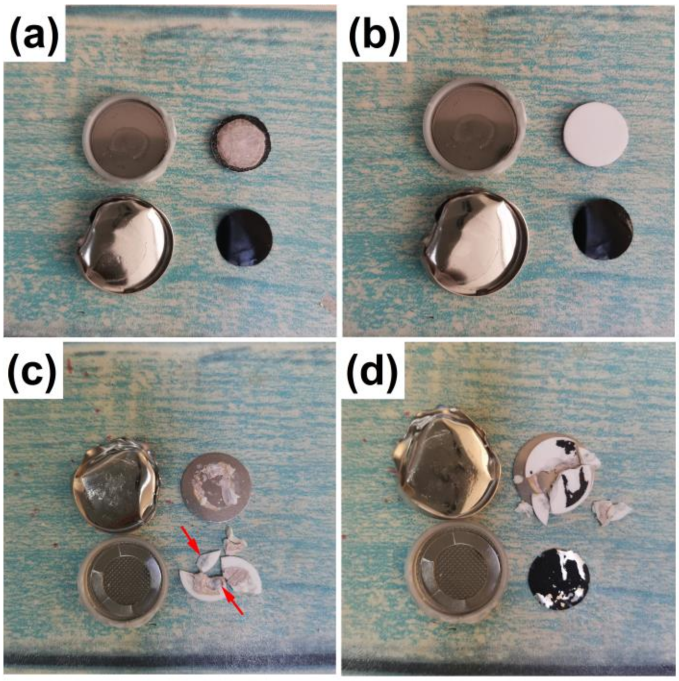

Fig. S6 Digital photographs of $Na_3V_2(PO_4)_3$ (LE)/BiO_x-modified NZSP/Na (a, b) and $Na_3V_2(PO_4)_3$ (LE) /NZSP/Na (c, d) after rate cycling at 30 ºC.

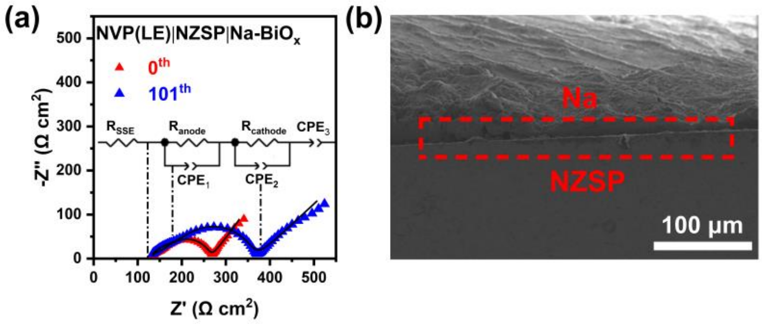

Fig. S7 (a) Impedance spectra and (b) cross-section SEM image of $Na_3V_2(PO_4)_3$ (LE)/BiO_x-modified NZSP/Na after 100 cycles at 1C with first cycle at 0.4C and 30 ºC.

Table S1. Performance comparison of symmetrical cells and full batteries.

Method	Symmetric cell		Full battery		Refs.
	CCD (mA cm^{-2})@(ºC)	Life(h)@*j*(mA cm^{-2})@temp. (ºC)	Capacity retention	Cycle No.	
TiO_2-$Na_3Zr_2Si_2PO_{12}$	N/A	0.1@RT@860 0.2@RT@750	70.6%	60	[2]
Sn/SnO_x-$Na_3Zr_2Si_2PO_{12}$	1.0@RT	0.1@RT@1500 0.3@RT@>500 0.5@RT@100	97.0%	100	[3]
SnS_2-$Na_3Zr_2Si_2PO_{12}$	0.9@RT	0.1@RT@800 0.25@RT@600 0.3@RT@400 0.4@RT @100	96.7%	100	[4]
FAC-$Na_{3.1}Zr_2Si_{2.1}P_{0.9}O_{12}$	N/A	0.1@75@100 0.2@75@100 0.3@75@100 0.4@75@100 0.5@75@100	96.4%	100	[5]
UW-$Na_3Zr_2Si_2PO_{12}$	0.6@RT	0.1@RT@1300 0.2@RT @400	89.8%	900	[6]
$BaTiO_3$-$Na_3Zr_2Si_2PO_{12}$	1.05@RT	0.1@RT@1000 0.2@RT @1000 0.3@RT @1000	84.4%	400	[7]
AlF_3-$Na_3Zr_2Si_2PO_{12}$	1.0@RT 1.2@60	0.15@60@150 0.25@60@150	83.4%	100	[8]
BiO_x-$Na_3Zr_2Si_2PO_{12}$	1.2@30	0.1@30@1000 0.5@30@1000	97.3%	100	This work

Supplementary references

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