Electronic Supplementary Information

Crystalline-iceplant-like nano-$NaVPO_4F$@graphene as an intercalation-type anode material for sodium-ion batteries

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Experimental

1.1 Synthesis of NVPFG

NVPFG was synthesized using a freeze-drying process as shown in Fig. 1. In brief, graphite oxide was obtained with the Hummers method.[1] Graphite oxide is exfoliated in water using ultrasonic waves to obtain graphene oxide (GO) solution. Stoichiometric amounts of NH_4VO_3, oxalic acid, $NH_4H_2PO_4$ and NaF were sequentially dissolved in water and kept at 50 °C to promote dissolution. After complete dissolution, the solution was added dropwise into the GO solution and persistently stirred. The mixture was then rapidly frozen in liquid N_2 and dried in a freeze dryer. The dry precursor was pre-sintered at 350 °C in an Argon atmosphere for 5 hours. After cooling to room temperature, the percursor was ground and sintered at 750 °C for 8 hours in Argon atmosphere to yield the NVPFG composite.

1.2 Materials characterizations

The crystalline structures of the composite and the electrodes after discharging and charging were characterized by X-ray diffraction (XRD) using an X-ray diffractometer (Bruker D8 Advance, Cu K_α radiation). Thermogravimetric analysis (TGA) was conducted in the air from room temperature to 800 °C under a heating rate of 10 °C min^{-1} using a thermal analyzer (TGA Q50). The Raman spectrum was taken by a Raman spectrometer (Renishaw-inVia, UK). The morphology of NVPFG was observed with a scanning electron microscope (SEM, Hitachi Su-70) and a transmission electron microscope (TEM, JEM-2100&X-Max80). X-ray photoelectron spectroscopy (XPS) were recorded by a Microlab 350 spectrometer employing a monochromatic Mg-K_α X-ray source.

1.3 Electrochemical measurements

The electrochemical characterization of NVPFG was evaluated using CR2032 coin-cells. A homogeneous slurry was obtained by mixing NVPFG, acetylene black (AB) and poly(vinylidene difluoride) (PVDF) in a weight ratio of 8:1:1 in N-methyl-2-pyrrolidone (NMP). This slurry was then coated on a copper foil and dried in an electric oven to obtain an electrode laminate. Afterwards, CR2032 half-cells were assembled in an argon-filled glove box (MBRAUN MB-Labstar 1500/780). The electrolyte was 1 M $NaClO_4$ in propylene carbonate (PC), while glass fiber (Whatman GF/D) was used as the separator. The coin-cells were evaluated on a Neware BTS-4008 multichannel battery test system within the voltage range of 0.01-2.70 V at different C rates (1 C= 143 mAh g^{-1}).

1 W.S. Hummers and R.E. Offeman Hummers, *J. Am. Chem. Soc.*, 1958, **80**, 1339.

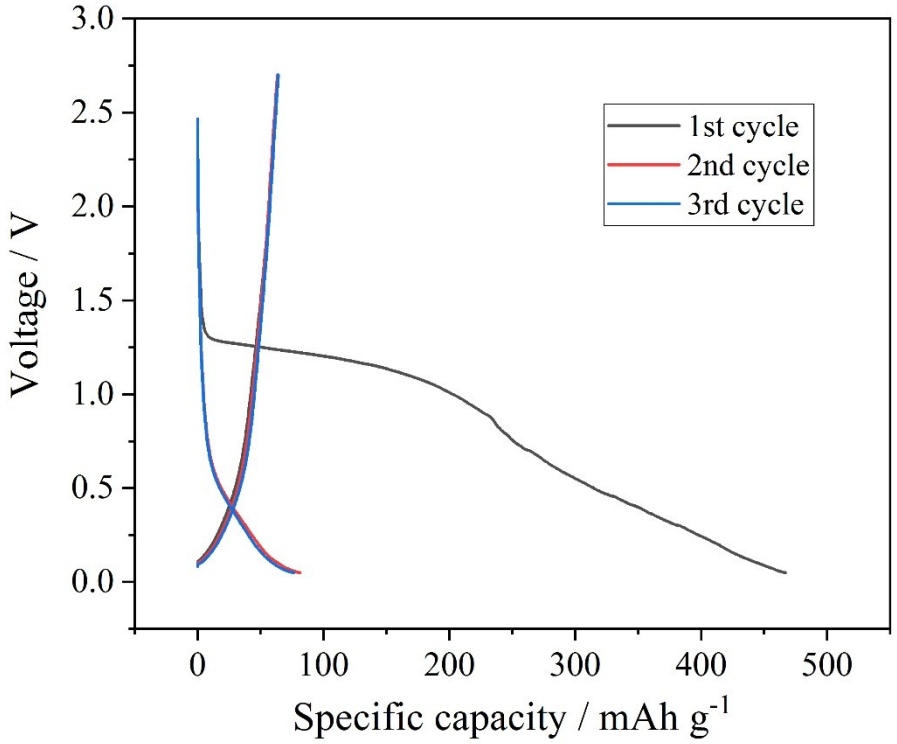

Fig. S1. Voltage profiles of acetylene black at 0.1 C.

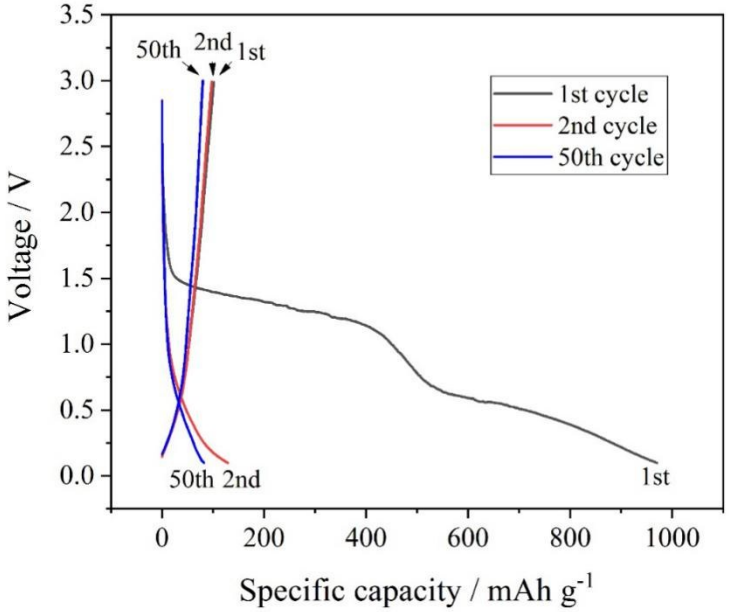

Fig. S2. Voltage profiles of graphene at 0.1 C.

Tab. S1. The specific capacity of the initial cycle.

	NVPF	graphene	Acetylene black	total
Mass ratio[a]	0.92	0.08	0.125	
Initial specific capacity / mAh g^{-1}	X	100	64	
Initial capacity / mAh g^{-1}	0.92X	8	8	148

a. the mass ratios are based on the mass of NVPFG.

So, the specific capacity (X) of NVPF in the initial cycle is calculated to be 143 mAh g^{-1}.