

## Electronic supporting information (ESI)

### Enhanced K-Ion Kinetics in a Layered Cathode for Potassium Ion Batteries

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## Experiments

### Material synthesis

Na<sub>0.9</sub>Cr<sub>0.9</sub>Ru<sub>0.1</sub>O<sub>2</sub>(NCRO) was prepared by multistep solid-state reaction. Na<sub>2</sub>CO<sub>3</sub> (5 wt% excess, 99.99 %, Sigma-Aldrich), Cr<sub>2</sub>O<sub>3</sub> (99.9 %, Sigma-Aldrich) and RuO<sub>2</sub>(99.9%, Sigma-Aldrich) were mixed and homogenized using a planetary ball mill at 300 rpm for 5 h. Then the powder mixture was pelletized, and the resulting pellet was heated at 750°C, 900 °C and 1000°C for 2~3 h at each step in Ar atmosphere. Then, the sample was naturally cooled and put into Ar-filled glove box for storage.

### Material characterization

Inductively coupled plasma atomic emission spectroscopy (ICP) measurement was conducted on Optima 5300DV. The XRD spectra of as-prepared samples were collected on a Bruker D8-Advanced with Cu K $\alpha$  radiation. Rietveld refinement was obtained using GSAS software. The particle morphology and size was observed by scanning electron microscopy (SEM, Hitachi SU8010) and Transmission electron microscope (TEM, FEI-TF20). Elements distribution was studied using electron diffraction spectroscopy (EDS). The chemical state of the samples was analyzed by X-ray photoelectron spectroscopy (XPS, Thermo Scientific ESCALAB 250 XI X-ray photoelectron spectrometer).

### Electrochemical measurements

Electrodes were prepared by mixing Na<sub>0.9</sub>Cr<sub>0.9</sub>Ru<sub>0.1</sub>O<sub>2</sub>, acetylene black and polyvinylidene fluoride (PVDF) binder (mass ratio of 7:2:1) with N-methyl-2-pyrrolidone (NMP) until the slurry become homogeneous. The homogeneous slurry was coated on the Al foil and dried at 120°C for 12h under vacuum. Coin-type half-cells (CR2032) were assembled in an Ar-filled glove box using K metal as a counter electrode. The electrolyte solution consists of 0.8 M KPF<sub>6</sub> in EC: DEC (volume ratio of 1:1). Galvanostatic charge-discharge tests and GITT tests were recorded by a Land BT 2001A battery test system at room temperature with the voltage range of 1.5-3.8 V (vs. K<sup>+</sup>/K). GITT was performed by a current pulse of 20 mA/g with a relax time of 4 hours. Chemical diffusion coefficients (*D*s) can be

calculated by the following equation,

$$D_S = \frac{4}{\pi\tau} \left( \frac{m_B V_m}{M_B S} \right)^2 \left( \frac{\Delta E_S}{\Delta E_\tau} \right)^2$$

where  $\tau$  is constant current pulse time,  $m_B$  and  $M_B$  are mass and molar mass of NCRO,  $V_m$  and  $S$  are molar volume and cathode surface area which contacts electrolyte.  $V_m$  is regard as a constant value during the charge and discharge process.  $\Delta E_S$  is the difference value of steady-state voltages after a current pulse, and  $\Delta E_\tau$  is the voltage change during a current pulse. <sup>1</sup> The specific capacities were normalized using mass of active material. And the cathode loading is about  $\sim 1\text{mg}/\text{cm}^2$ .

**Table S1 | Refinement results of initial NCRO sample**

<b>Phase</b>	<b>O3-type</b>	
<b>Space Group</b>	<b>R <math>\bar{3}</math> m</b>	
<b>Cell parameters</b>	a (Å)	2.9605(8)
	b (Å)	2.9605(8)
	c (Å)	16.2334(5)
	$\alpha$ (°)	90
	$\beta$ (°)	90
<b>Cell parameters</b>		
<b>Agreement factors</b>	$\gamma$ (°)	120
	Volume (Å <sup>3</sup> )	123.22(4)
	R <sub>wp</sub> (%)	8.28
	R <sub>p</sub> (%)	5.30
<b>CHI</b>		9.067

**Table S2 | Refinement results of NCRO sample after 1st discharge**

<b>Phase</b>		O3-type	P3-type
<b>Space Group</b>		R $\bar{3}$ m	R 3m
<b>Cell parameters</b>	a (Å)	2.9617(7)	2.9560(9)
	b (Å)	2.9617(7)	2.9560(9)
	c (Å)	16.0924(6)	18.7226(2)
	$\alpha$ (°)	90	90
	$\beta$ (°)	90	90
<b>Cell parameters</b>	$\gamma$ (°)	120	120
<b>Agreement factors</b>	Volume (Å <sup>3</sup> )	122.25(2)	141.68(8)
	R <sub>wp</sub> (%)	6.35	
	R <sub>p</sub> (%)	4.13	
<b>CHI</b>		9.755	

Table S3 | Refinement results of NCRO sample after 400th discharge

Phase		P3-type
<b>Space Group</b>		R 3m
	a (Å)	2.9722(5)
	b (Å)	2.9722(5)
	c (Å)	19.2554(8)
	$\alpha$ (°)	90
<b>Cell parameters</b>	$\beta$ (°)	90
	$\gamma$ (°)	120
	Volume (Å <sup>3</sup> )	147.41(3)
	R <sub>wp</sub> (%)	8.20
<b>Agreement factors</b>	R <sub>p</sub> (%)	5.22
<b>CHI</b>		7.684

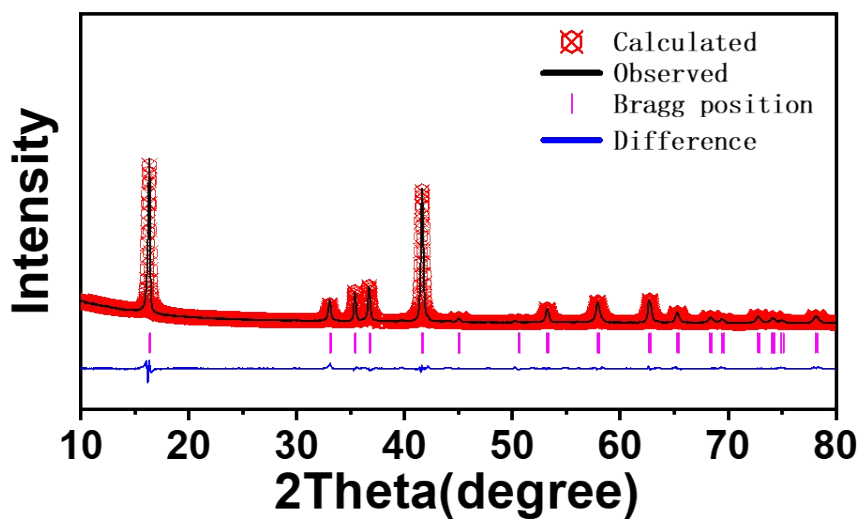


Fig. S1 Riveted-refined XRD profile of NCRO.

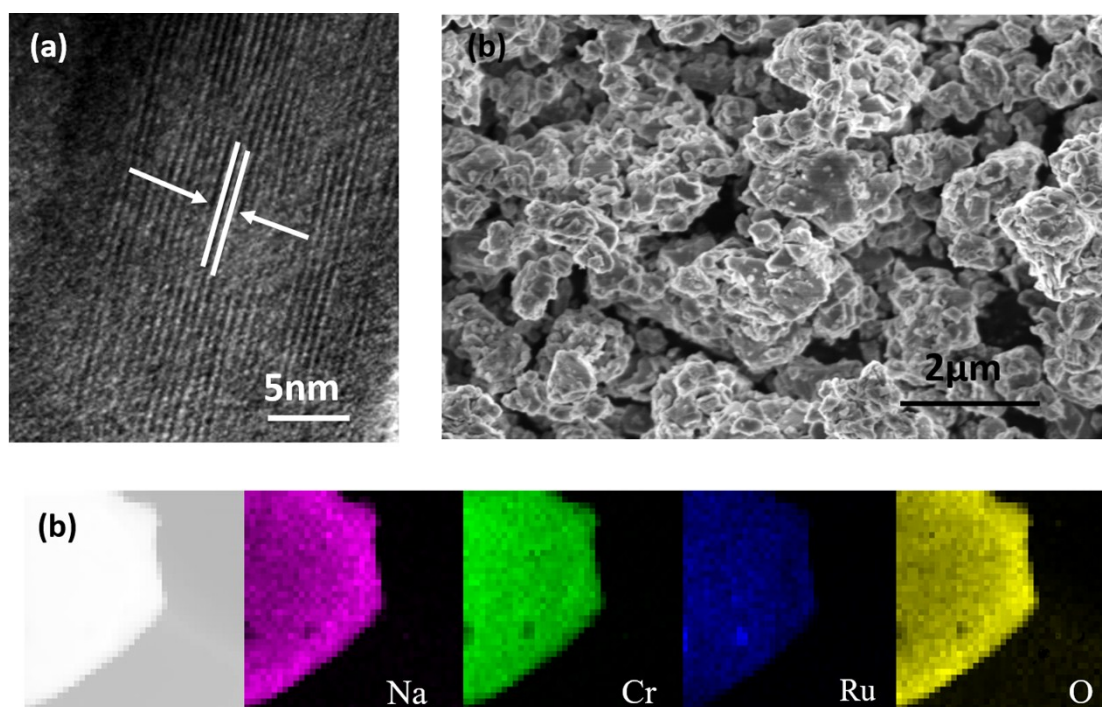


Fig.S2 (a) TEM image of a single nanobelt showing an interlayer spacing of 0.569nm;(b) SEM image of NCRO;(c) TEM and corresponding element mapping of Na, Cr, Ru and O.

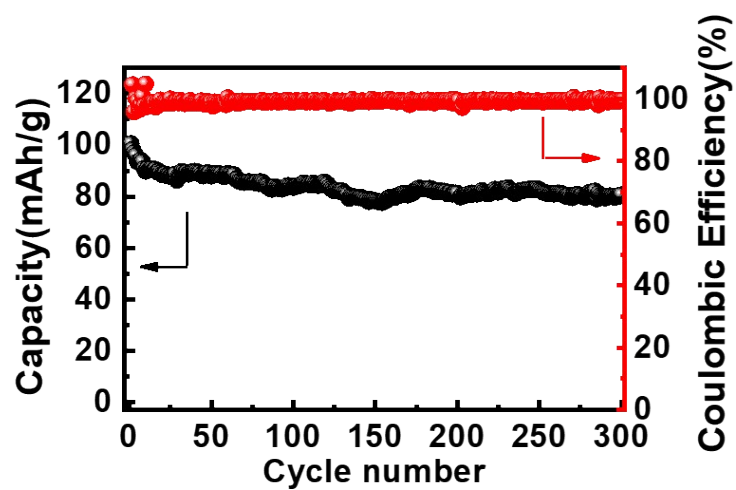


Fig. S3 Cycling performance of NCRO at 0.5C.

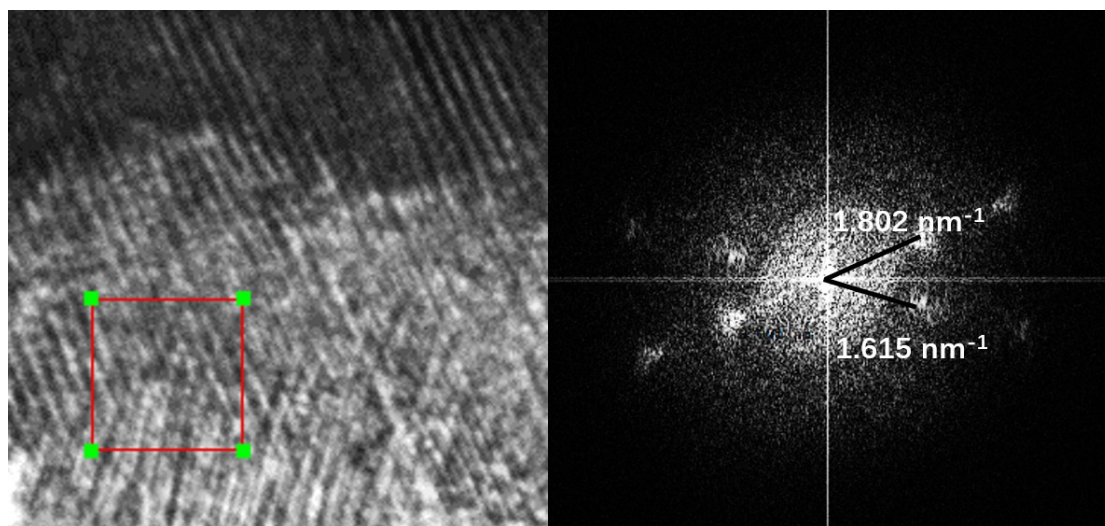
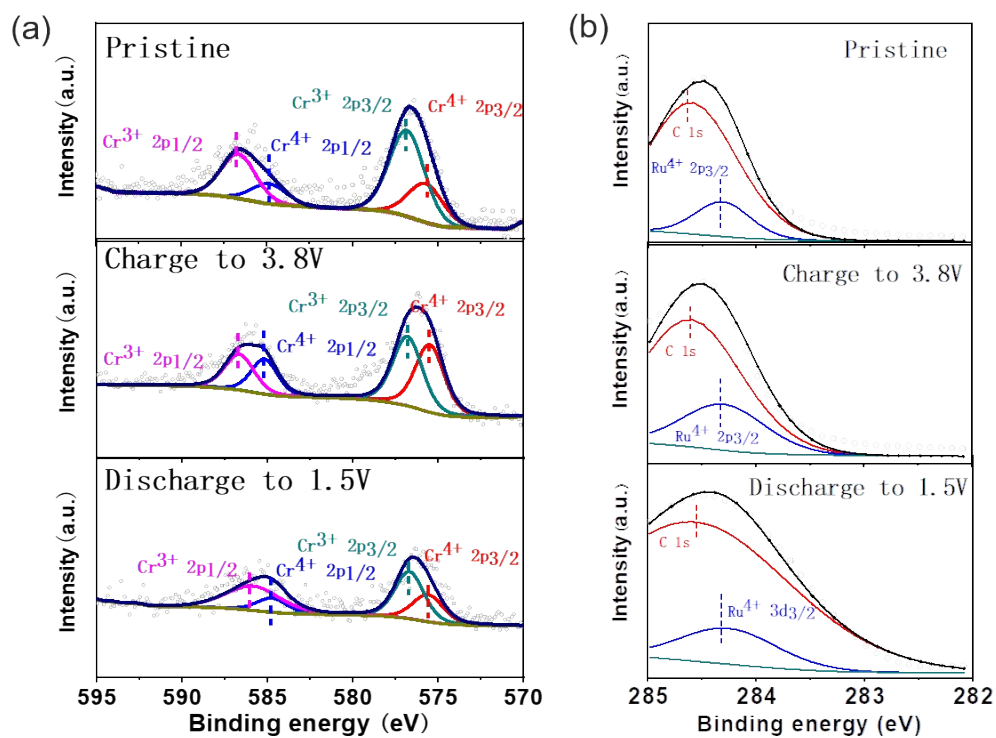


Fig S4. TEM and corresponding FFT image of discharged NCRO from the red square area.



**Fig S5.** XPS spectra of (a) Cr 2p and (b) Ru 3d<sub>3/2</sub> of NCRO, charged NCRO and discharged NCRO.

1. C. J. Wen, B. Boukamp, R. A. Huggins and W. Weppner, *Journal of The Electrochemical Society*, 1979, **126**, 2258–2266.