Supporting Information

Exceptionally large energy cathode with K-SO_4-Cu conversion reaction for potassium rechargeable batteries

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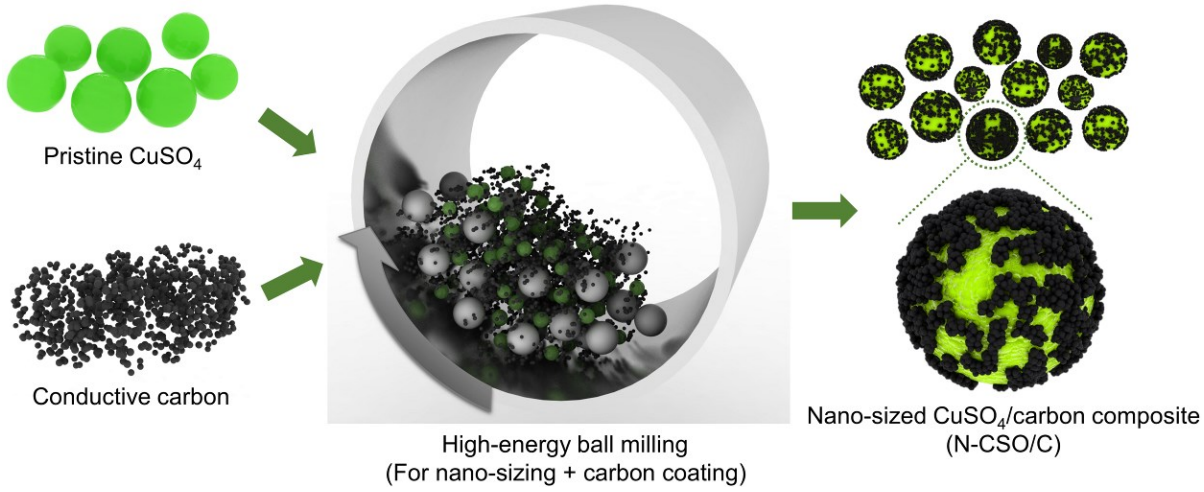

Fig. S1 Scheme of preparation of N-CSO/C using high-energy ball milling

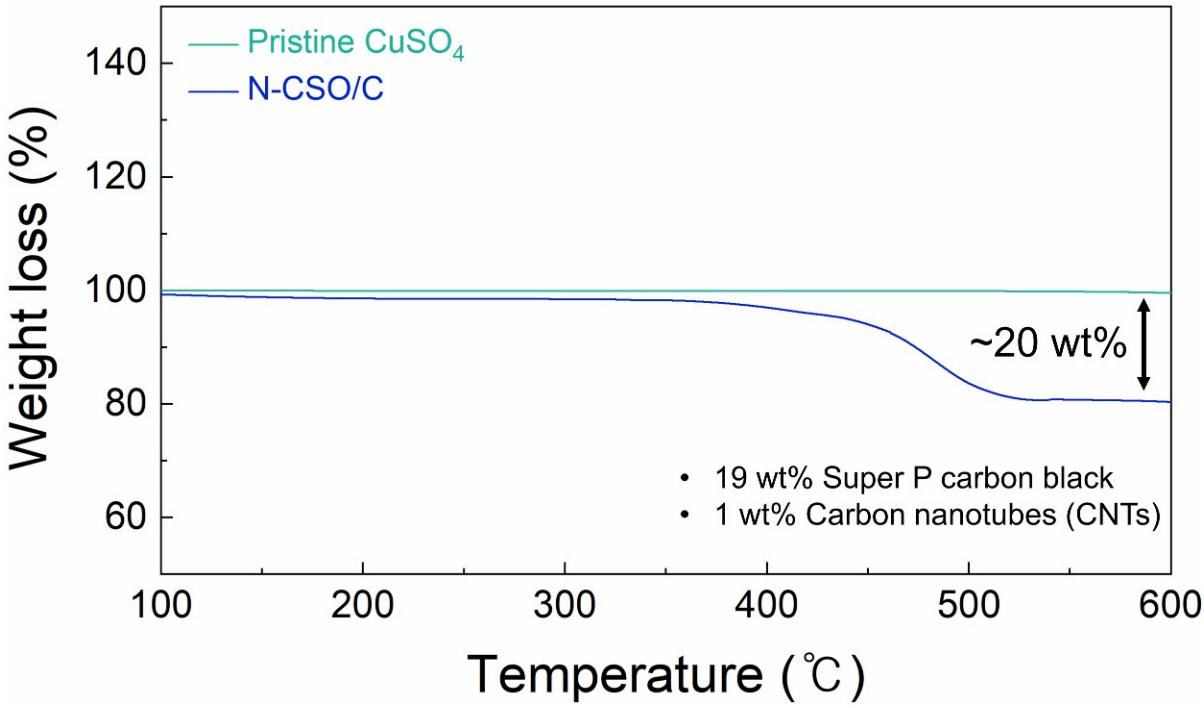

Fig. S2 Thermogravimetric (TGA) spectra profiles of pristine $CuSO_4$ and N-CSO/C composite

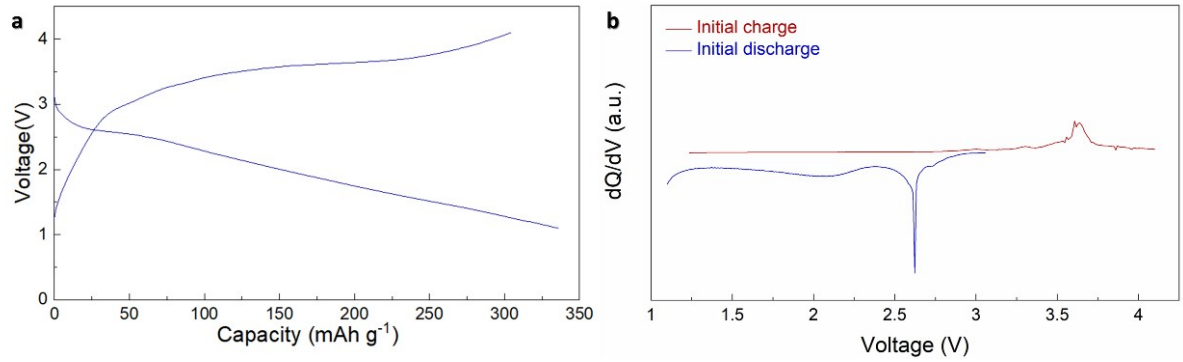

Fig. S3 (a) Charge/discharge curve, (b) differential capacity (dQ/dV) of initial cycle of N-CSO/C at current rate of 12 mA g^{-1} in the voltage range of 1.1-4.1 V (*vs*. K^+/K)

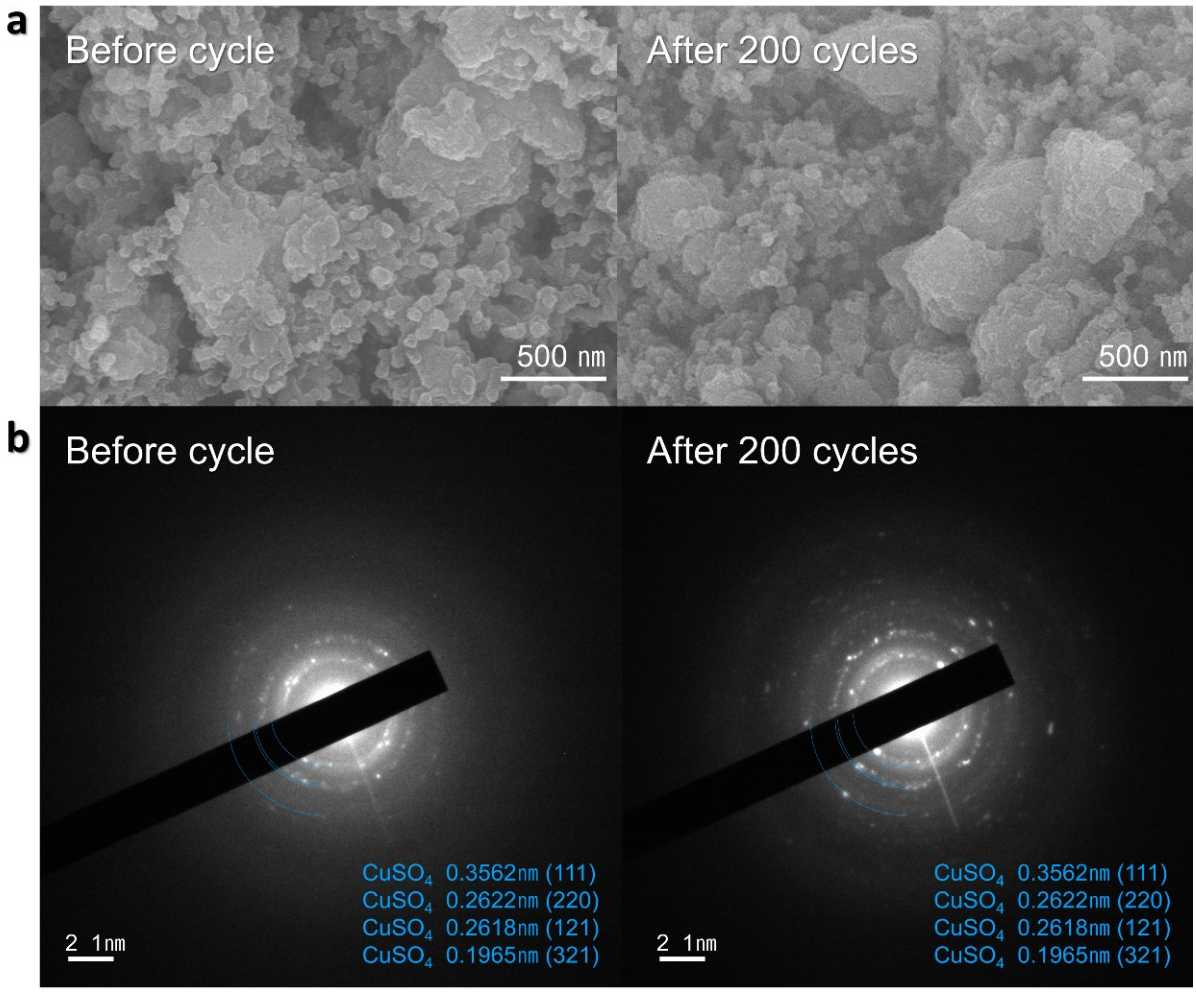

Fig. S4 Comparing (a) SEM images, (b) SAED patterns of N-CSO/C before cycle and after 200 cycles

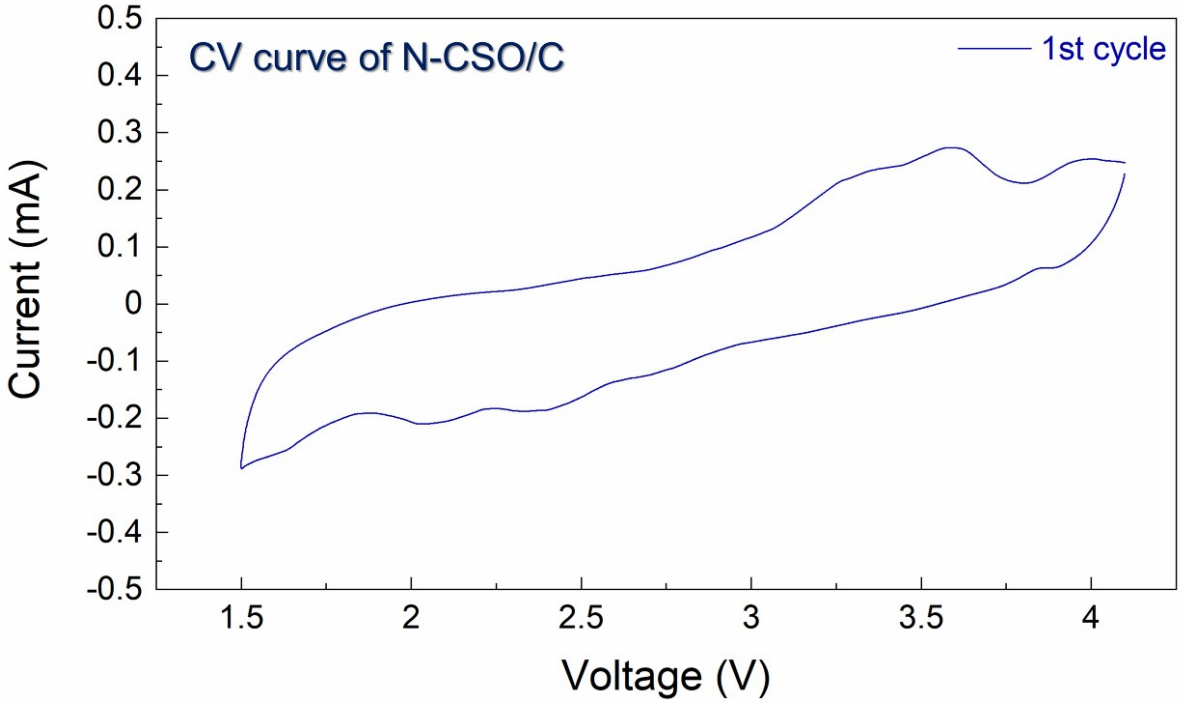

Fig. S5 CV profiles of the N-CSO/C electrode measured at 1 mV s^{-1} .

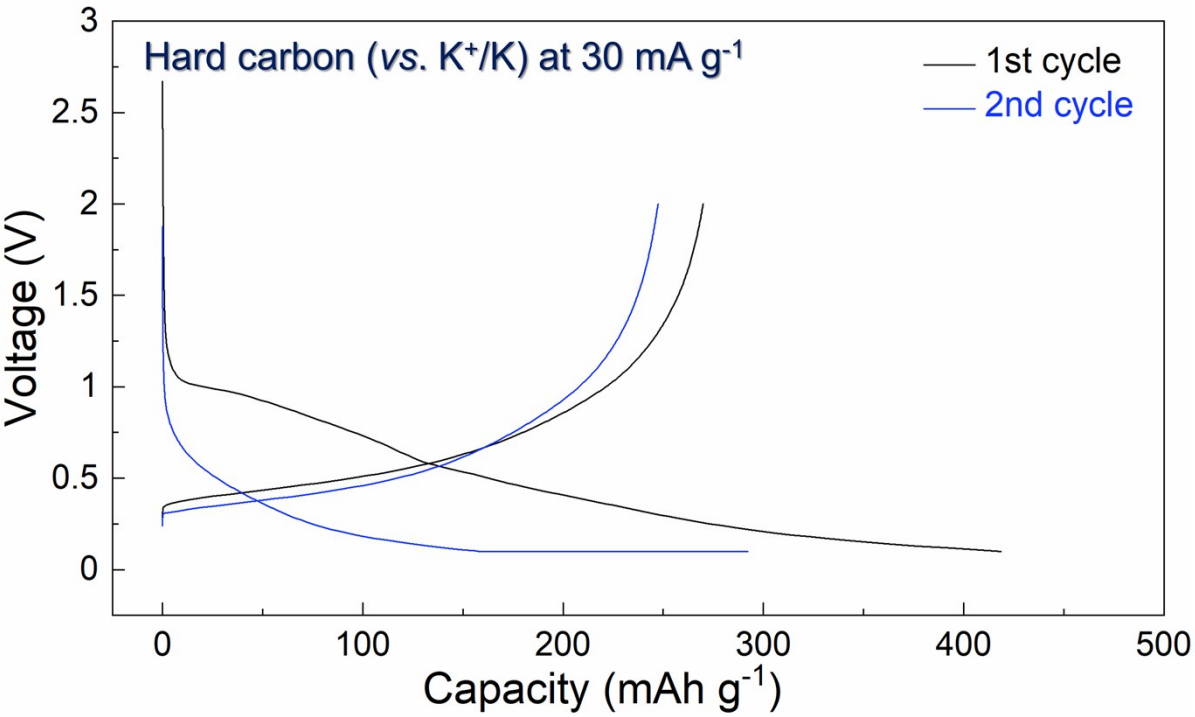

Fig. S6. Charge/discharge curves of one- and two-times pre-cycled hard carbon in the voltage range of 0.01-2.0 V (*vs*. K^+/K) at 30 mA g^{-1}

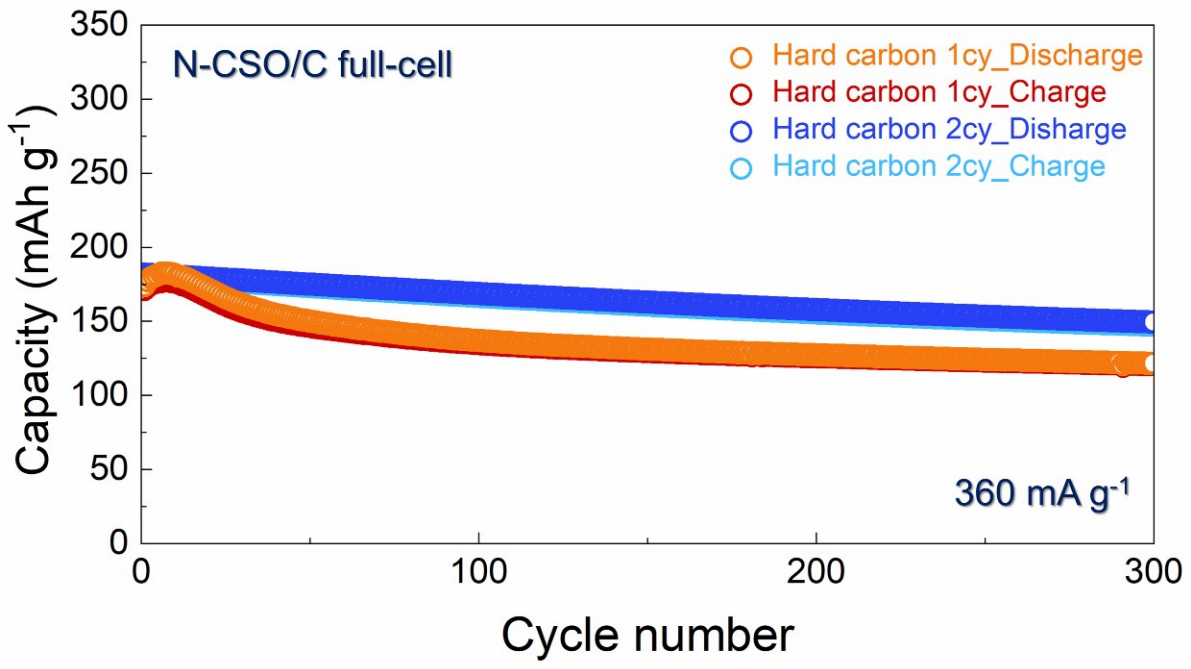

Fig. S7. Cycle performances of N-CSO/C-based full-cell using one- and two-times pre-cycled hard carbon in the voltage range of 0.01-2.0 V (*vs*. K^+/K) at 30 mA g^{-1}.

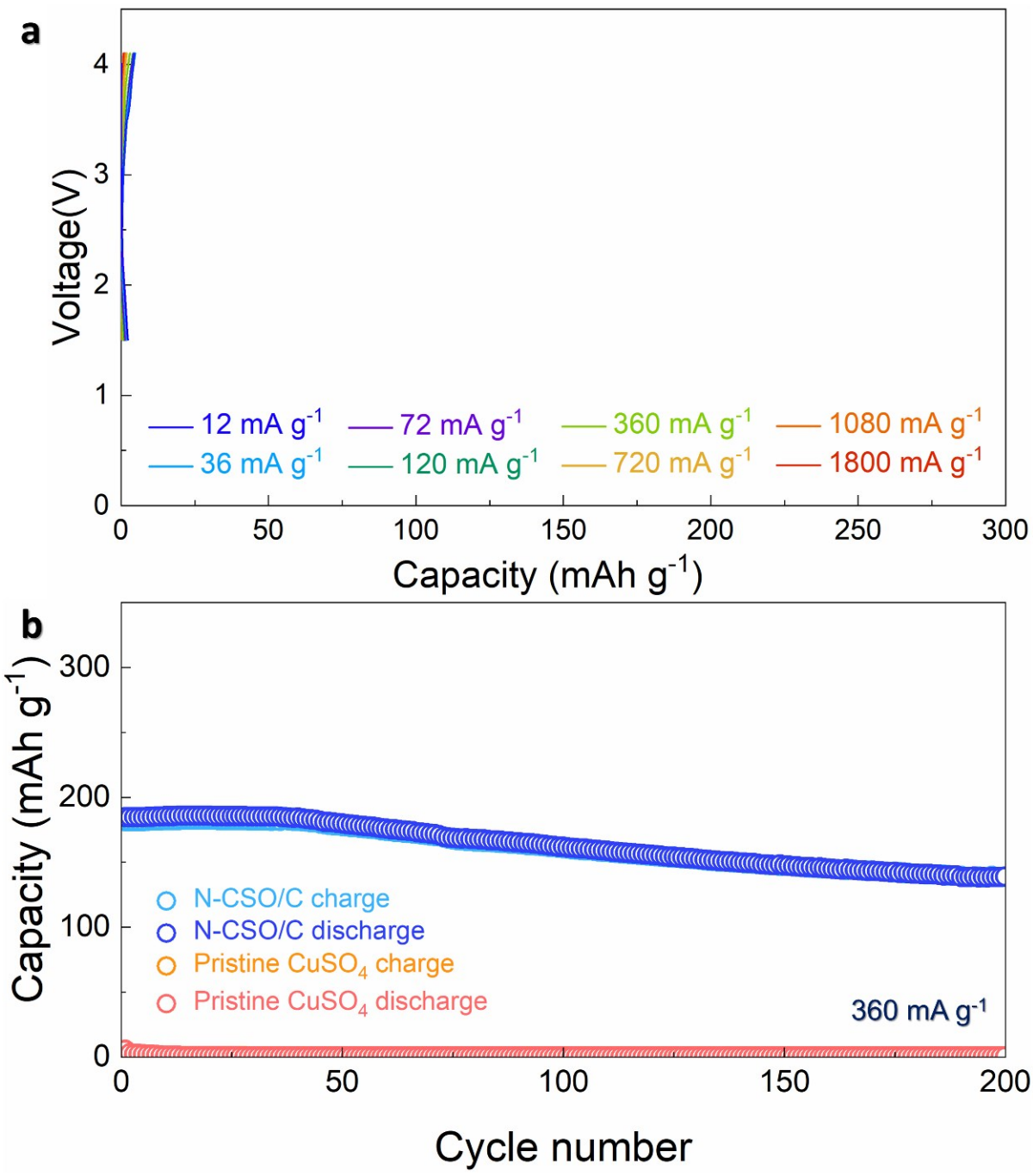

Fig. S8 (a) Charge/discharge curves of pristine $CuSO_4$ at various current rates (b) Comparing cyclic performance between pristine $CuSO_4$ and N-CSO/C during 200 cycles at 360 mA g^{-1} after 1 cycle at 120 mA g^{-1}

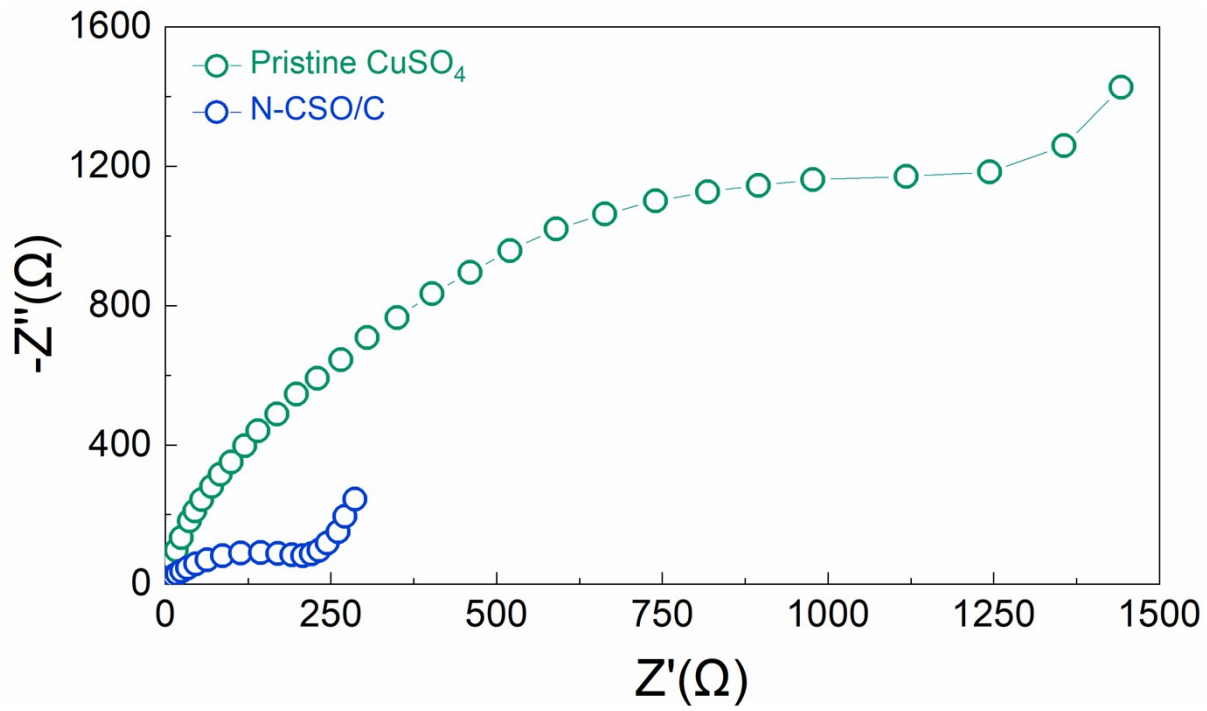

Fig. S9 Electrochemical impedance spectra profiles of pristine $CuSO_4$ and N-CSO/C composite

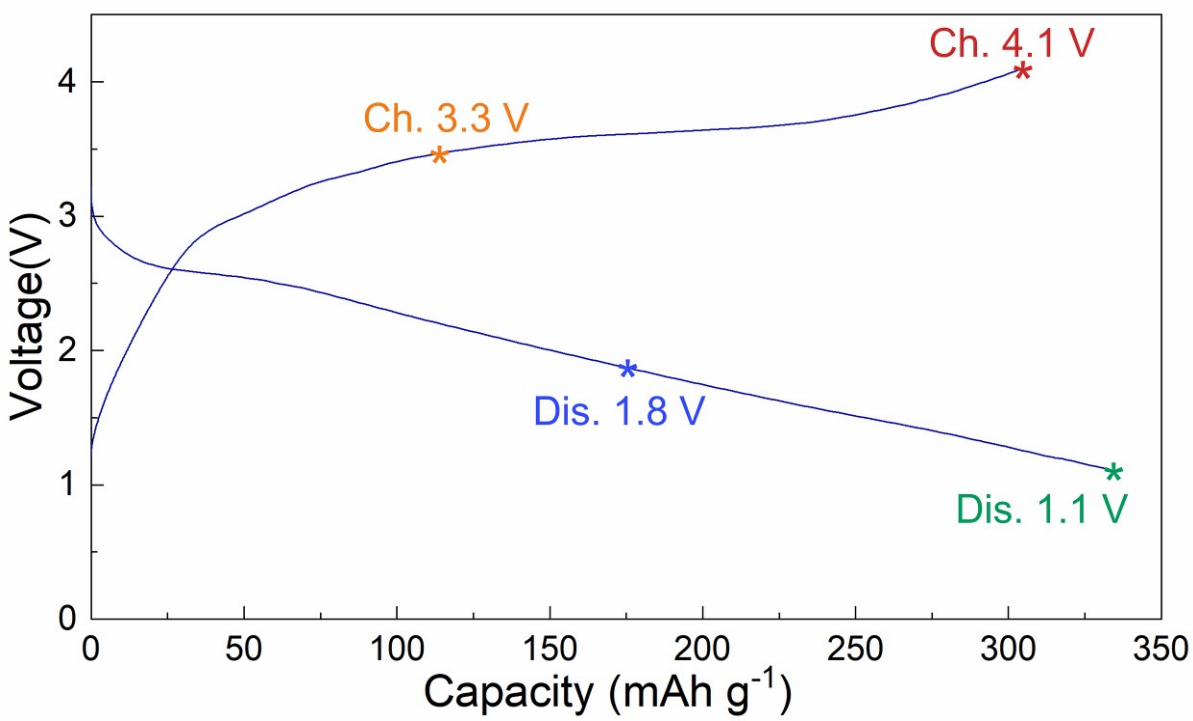

Fig. S10 Each voltage points of preparation samples on charge/discharge curve of N-CSO/C for *operand/ex-situ* XRD, ToF-SIMS, XANES and EXAFS measurements

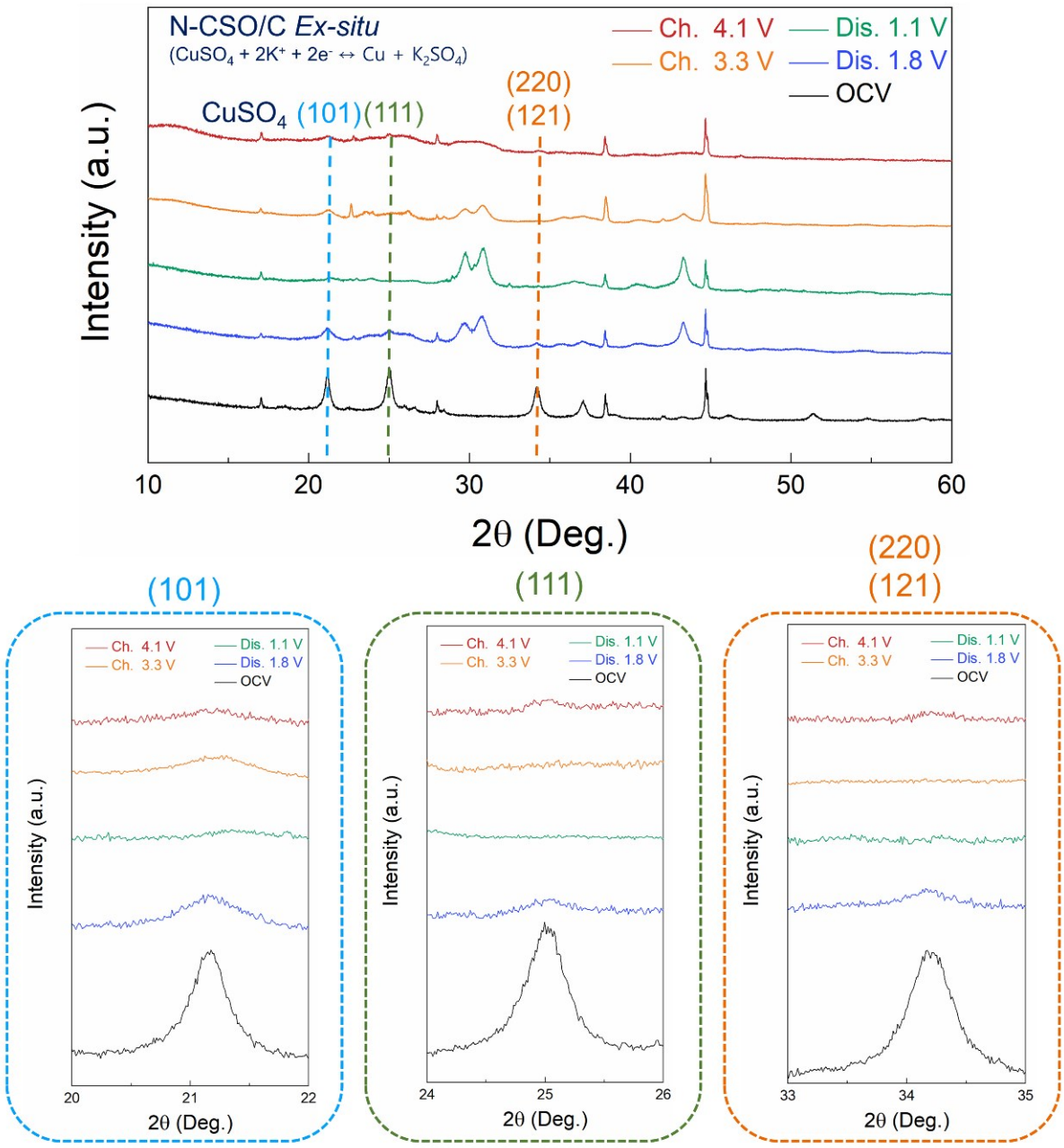

Fig. S11 Ex-situ XRD patterns of N-CSO/C electrodes with the expanded regions

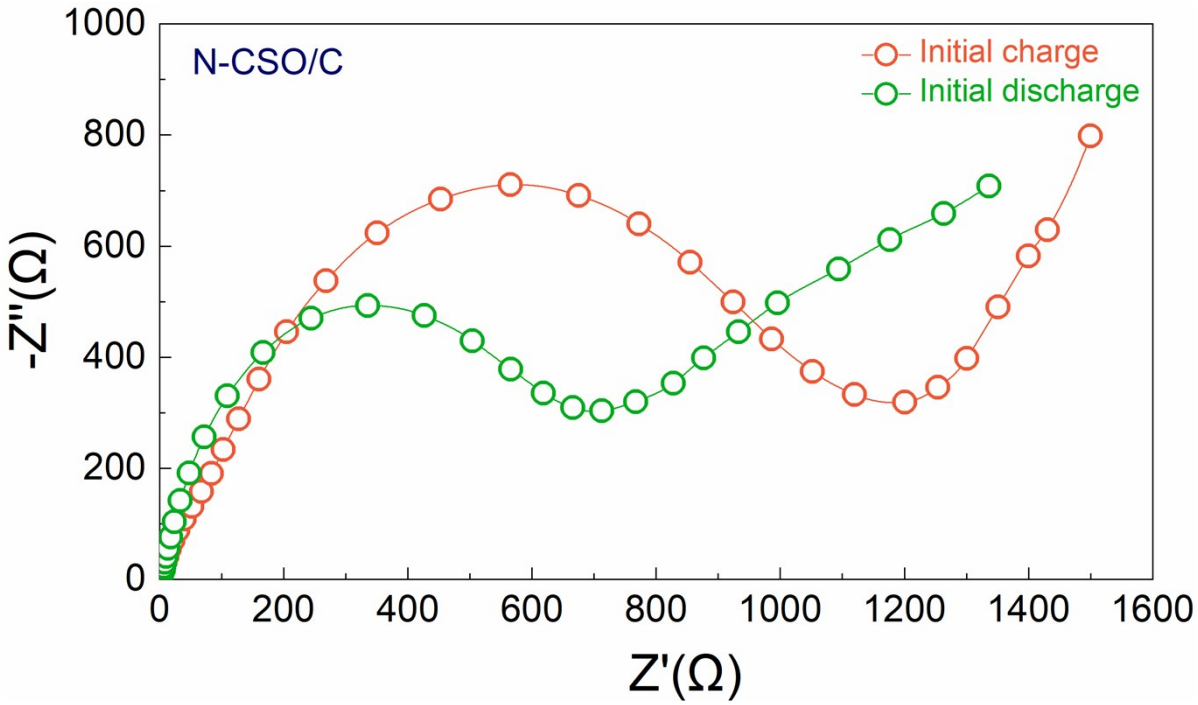

Fig. S12 Electrochemical impedance spectra profiles of fully charged/discharged N-CSO/C electrode

Table S1 (a) Predicted theoretical redox potentials of $CuSO_4$ and CuO using first principles calculation (b) Formation energies of $CuSO_4$, K_2SO_4, Cu and K obtained by first principles calculation

a

$CuSO_4$(*vs*. K^+/K): $CuSO_4 + 2K^+ + 2e^- \leftrightarrow Cu + K_2SO_4$		
Compound	Final E/atom (eV/f.u.)	Final E (eV/f.u.)
$CuSO_4$	-5.7117	-34.2702
2K	-1.1103	-2.6226
K_2SO_4	-5.6185	-39.3295
Cu	-4.0993	-4.0993
Theoretical voltage of $CuSO_4$: -3.268 (vs. K^+/K)		

CuO(*vs*. K^+/K): $CuO + 2K^+ + 2e^- \leftrightarrow Cu + K_2O$		
Compound	Final E/atom (eV/f.u.)	Final E (eV/f.u.)
CuO	-4.9490	-9.8980
2K	-1.1103	-2.6226
K_2O	-3.3780	-10.134
Cu	-4.0993	-4.0993
Theoretical voltage of CuO : -1.7127 (vs. K^+/K)		

b

Compound	Formation energy (eV/f.u.)
$CuSO_4$	-34.2702
K_2SO_4	-39.3295
Cu	-3.75383
K	-1.1103

Table S2 Comparison of theoretical voltage of $CuSO_4$ corresponding to counter metal of Na, Mg and K

Counter metal	Conversion reaction	Theoretical voltage
Na	$CuSO_4 + 2Na^+ + 2e^- \leftrightarrow Cu + Na_2SO_4$	3.195 V (*vs*. Na^+/Na)
Mg	$CuSO_4 + Mg^{2+} + 2e^- \leftrightarrow Cu + MgSO_4$	2.775 (*vs*. Mg^{2+}/Mg)
K	$CuSO_4 + 2K^+ + 2e^- \leftrightarrow Cu + K_2SO_4$	3.268 V (*vs*. K^+/K)

Table S3 Lattice parameters of pristine $CuSO_4$

Sample	a (Å)	b (Å)	c (Å)	A (°)	B (°)	γ (°)	Volume ($Å^3$)
$CuSO_4$	8.479	6.754	4.957	90.0000	90.00	90.0000	283.87

Table S4 Comparison of electrochemical performances with previously reported various full cells for PRBs

Cathode material	Anode material	Electrolyte	Initial capacity (Current density)	Cycle retention	Voltage range (V)	Ref.
$CuSO_4$	Hard carbon	0.5 M KPF_6 in EC:DEC (1:1, v:v)	202 mAh g^{-1} (360 mA g^{-1})	85 % after 300 cycle	1.0-4.0	This work
P2-type $K_{0.6}CoO_2$	Hard carbon	0.9 M KPF_6 in EC:DEC (1:1, v:v)	71 mAh g^{-1} (30 mA g^{-1})	80 % after 100 cycle	0.5-3.8	41
P3-type $K_{0.5}[Mn_{0.8}Fe_{0.1}Ni_{0.1}]O_2$	Hard carbon	0.5 M KPF_6 in EC:DEC (1:1, v:v)	113 mAh g^{-1} (30 mA g^{-1})	89 % after 150 cycle	0.5-3.6	36
$K_2V_3O_8$	Hard carbon	0.5 M KPF_6 in EC:DEC (1:1, v:v)	61 mAh g^{-1} (20 mA g^{-1})	87 % after 50 cycle	0.5-3.8	42
$K_{0.3}MnO_2$	Hard carbon /Carbon black composite	1.5 M KFSI in EC:DEC (1:1, v:v)	90 mAh g^{-1} (32 mA g^{-1})	50 % after 100 cycle	0.5-3.4	37
$K_{0.7}Fe_{0.5}Mn_{0.5}O_2$	Soft carbon	0.8 M KPF_6 in EC:DEC (1:1, v:v)	48 mAh g^{-1} (100 mA g^{-1})	76 % after 250 cycle	0.5-3.5	16
$K_{0.220}Fe[Fe(CN)_6]_{0.805}\cdot 4.01H_2O$	Super P	0.8 M KPF_6 in EC:DEC (1:1, v:v)	65 mAh g^{-1} (100 mA g^{-1})	93 % after 50 cycle	1.0-3.8	43
$K_{0.69}CrO_2$	Graphite	1.0 M KFSI, 6 wt % DTD in PC	78 mAh g^{-1} (100 mA g^{-1})	54 % after 100 cycle	0.8-3.8	44