

## Supporting Information

### **Copper Surface Doping to Improve Structure and Surface Properties of Manganese-Rich Cathode Materials for Sodium Ion Batteries**

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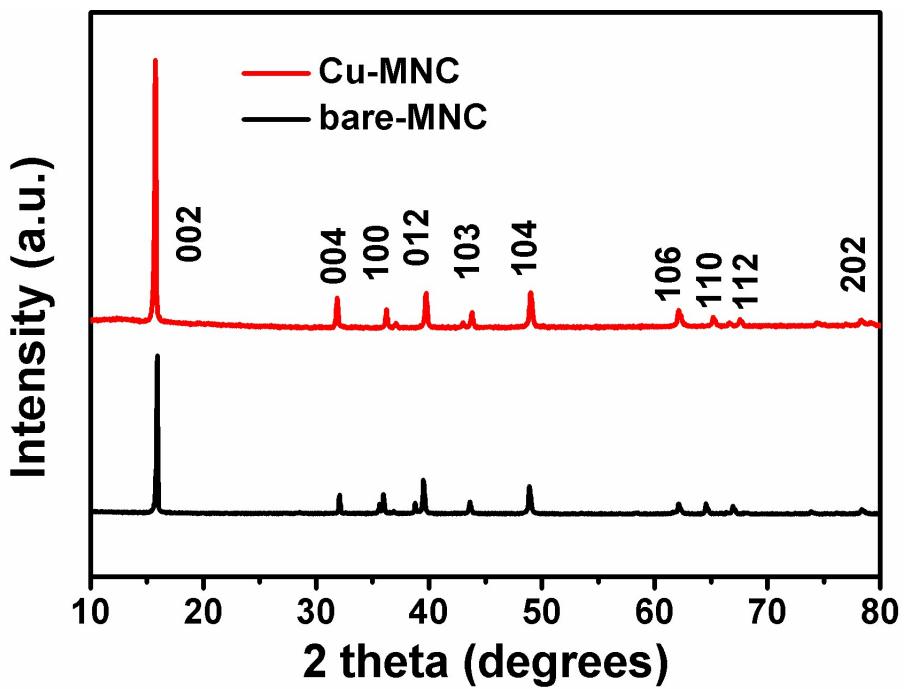


Figure S1 XRD patterns of Cu-MNC and bare-MNC samples.

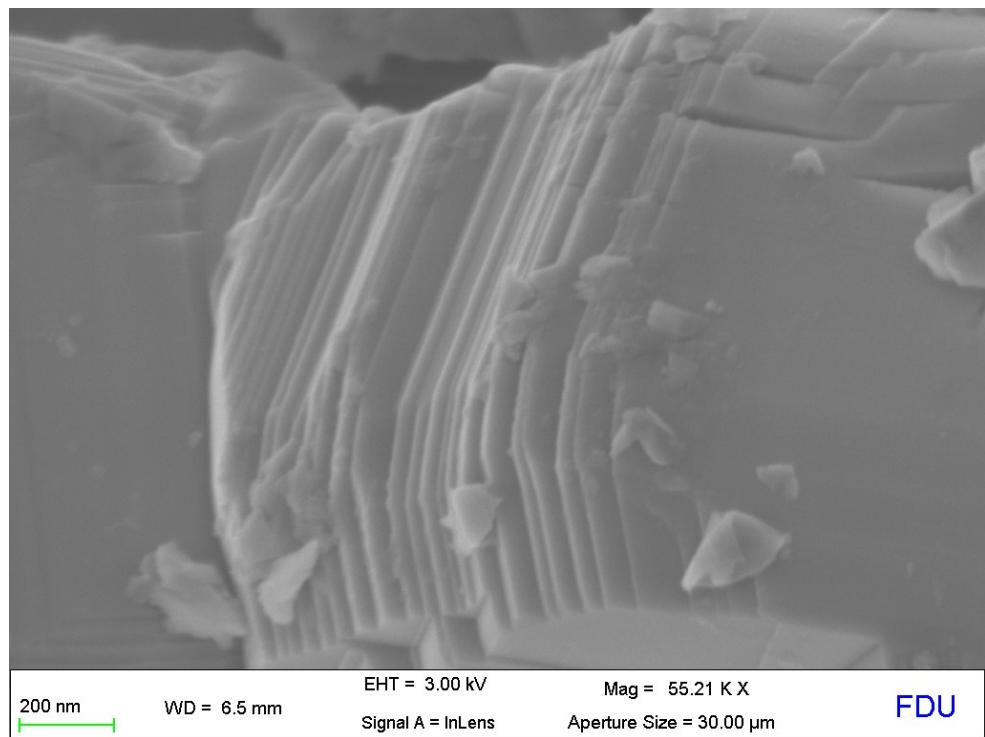


Figure S2. SEM image of Cu-MNC sample.

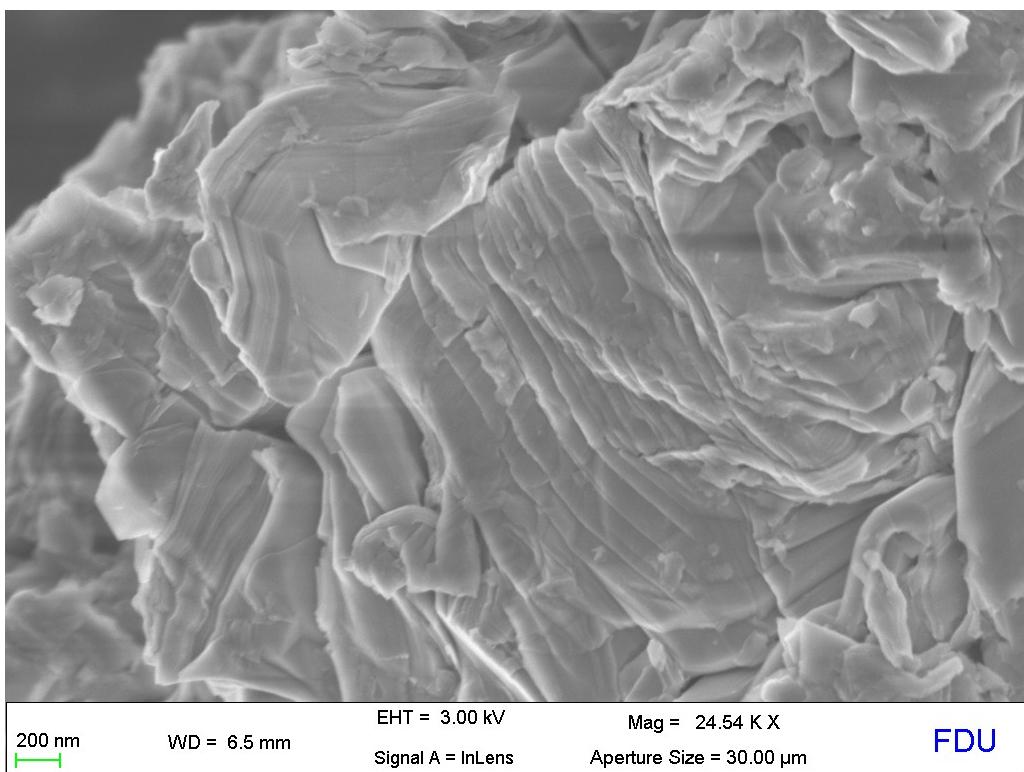


Figure S3. SEM image of bare-MNC sample.

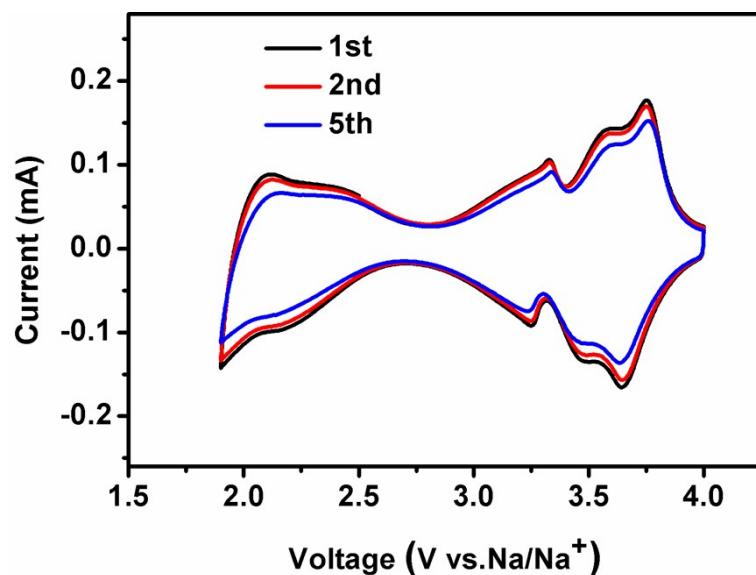


Figure S4. CV curves of bare-MNC at 0.2 mV/s for different cycles.

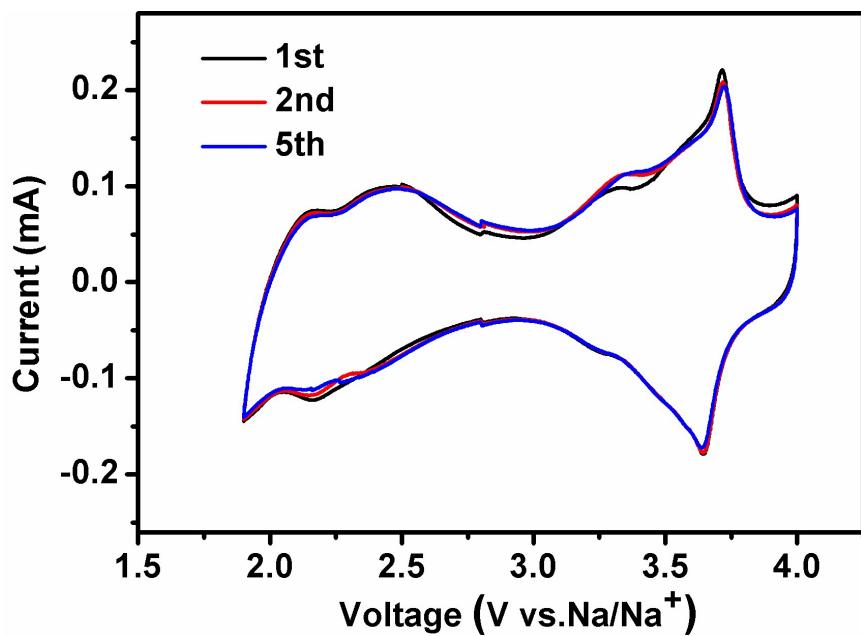


Figure S5. CV curves of Cu-MNC for different cycles.

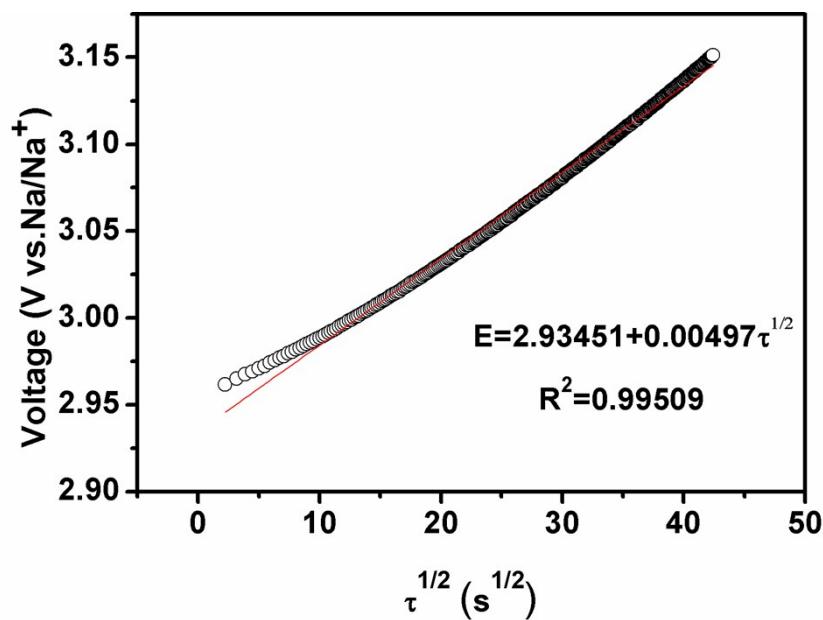


Figure S6. A linear relationship between the cell voltage and  $\tau^{1/2}$  for bare-MNC.

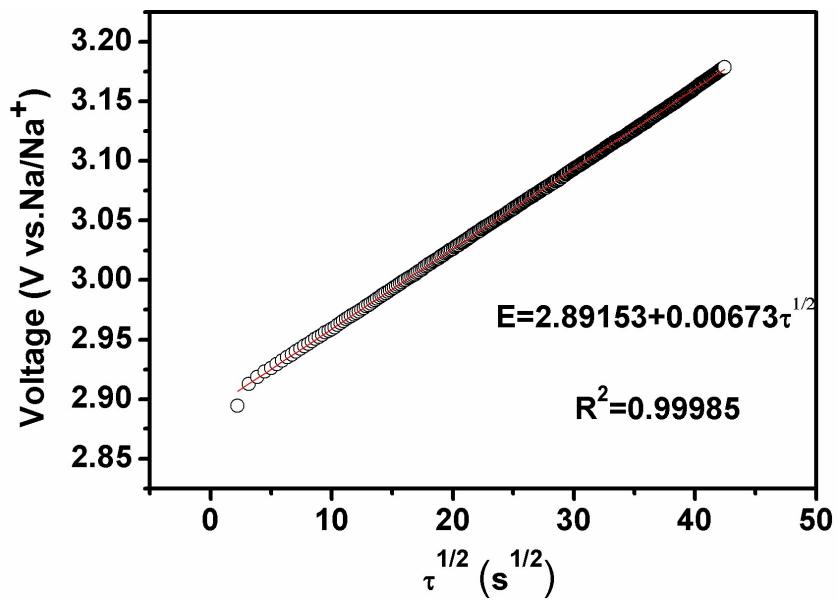


Figure S7. A linear relationship between the cell voltage and  $\tau^{1/2}$  for Cu-MNC.

Table S1. ICP results for the samples.

samples	Measured atomic ratio				
	Na	Mn	Ni	Co	Cu
1	Bare-MNC	0.6835	0.6025	0.1953	0.2022
2	Cu-MNC	0.6795	0.5934	0.2014	0.1902
					0.016

**Table S2.** Crystallographic parameters of bare-MNC refined by the Rietveld method.

Atom	P6 <sub>3</sub>		y	z	Occupancy
	/mmc(No.194)	site			
Na <sub>f</sub>	2b	0	0	0.25	0.35
Na <sub>e</sub>	2d	0.6667	0.3333	0.25	0.32
Mn	2a	0	0	0	0.6
Ni	2a	0	0	0	0.2
Co	2a	0	0	0	0.2
O	4f	0.6667	0.3333	0.079	0.975

a=b=2.8557(2)Å, c=11.2093(6)Å,  $\alpha = \beta = 90$ ,  $\gamma = 120$ , Rp=3.36 % Rwp=5.54 %  $\chi^2$ =3.08

**Table S3.** Crystallographic parameters of Cu-MNC refined by the Rietveld method.

Atom	P6 <sub>3</sub>		y	z	Occupancy
	/mmc(No.194)	site			
Na <sub>f</sub>	2b	0	0	0.25	0.35
Na <sub>e</sub>	2d	0.6667	0.3333	0.25	0.32
Mn	2a	0	0	0	0.584
Ni	2a	0	0	0	0.2
Co	2a	0	0	0	0.2
Cu	2a	0	0	0	0.016
O	4f	0.6667	0.3333	0.079	0.975

a=b=2.8569(9)Å, c=11.1772(6)Å,  $\alpha = \beta = 90$ ,  $\gamma = 120$ , Rp=4.39 % Rwp=5.39 %  $\chi^2$ =7.84

**Table S4** Fitting parameters for the equivalent circuit model.

Cycle number	bare-MNC			Cu-MNC		
	$R_\Omega$ ( $\Omega$ )	$R_f$ ( $\Omega$ )	$R_{ct}$ ( $\Omega$ )	$R_\Omega$ ( $\Omega$ )	$R_f$ ( $\Omega$ )	$R_{ct}$ ( $\Omega$ )
0	2.553	277.5	22.78	3.35	245.2	35.43
50	4.336	389.2	180.3	4.86	353.6	112.5