Supplementary Material

MgF_2 surface loading stabilizes the interfacial chemical environment of O3-Type $NaNi_{1/3}Fe_{1/3}Mn_{1/3}O_2$ cathodes for sodium-ion batteries

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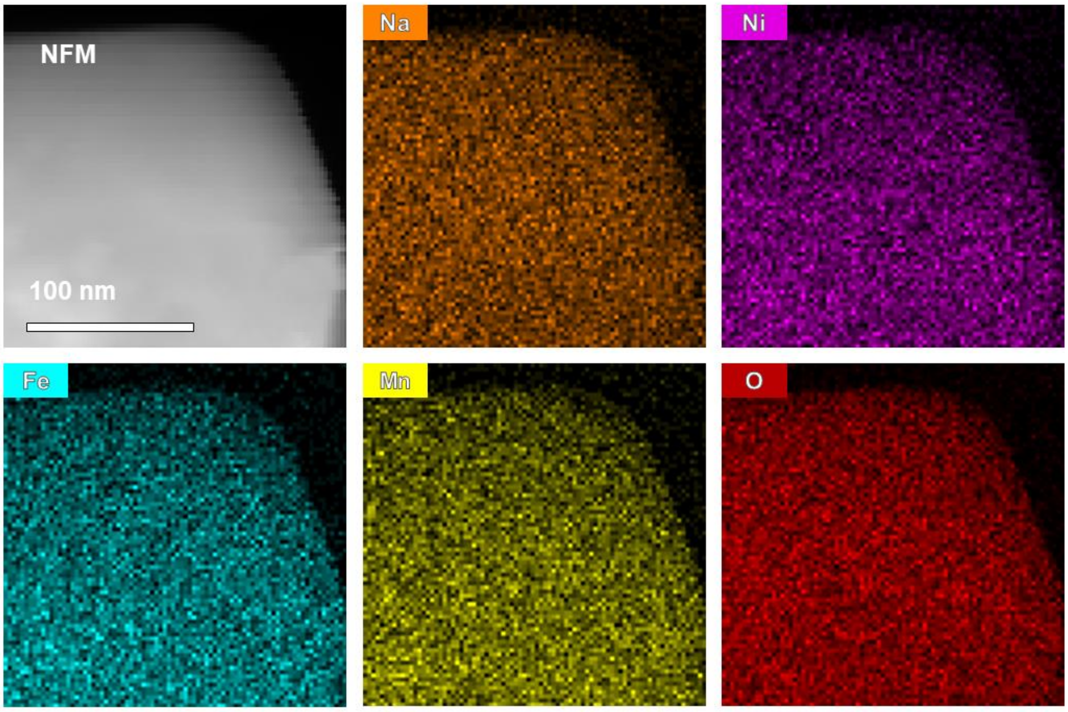
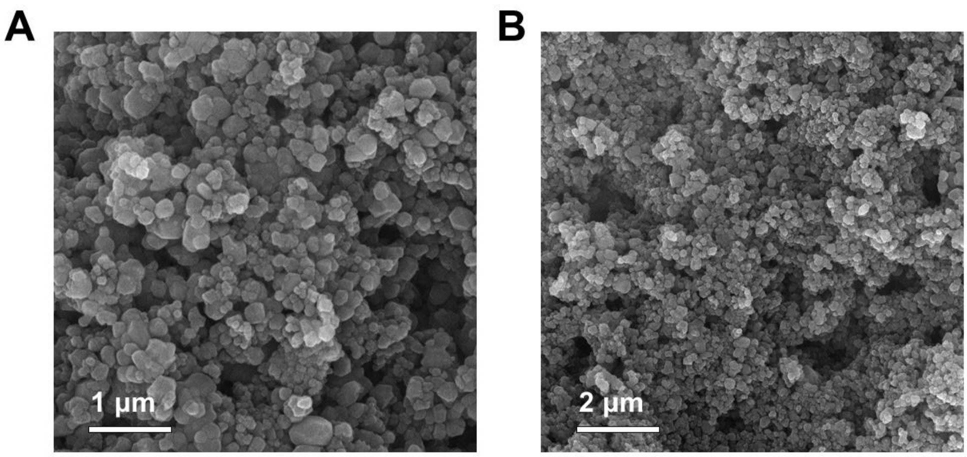
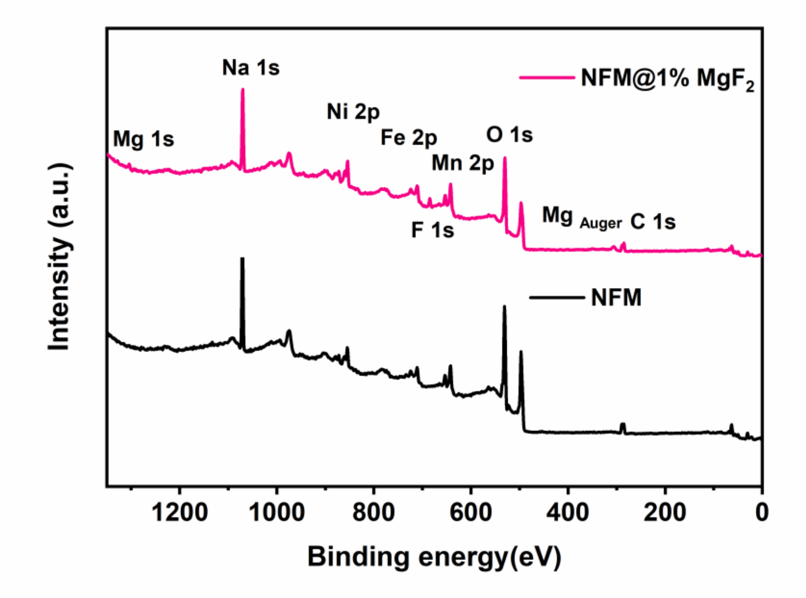


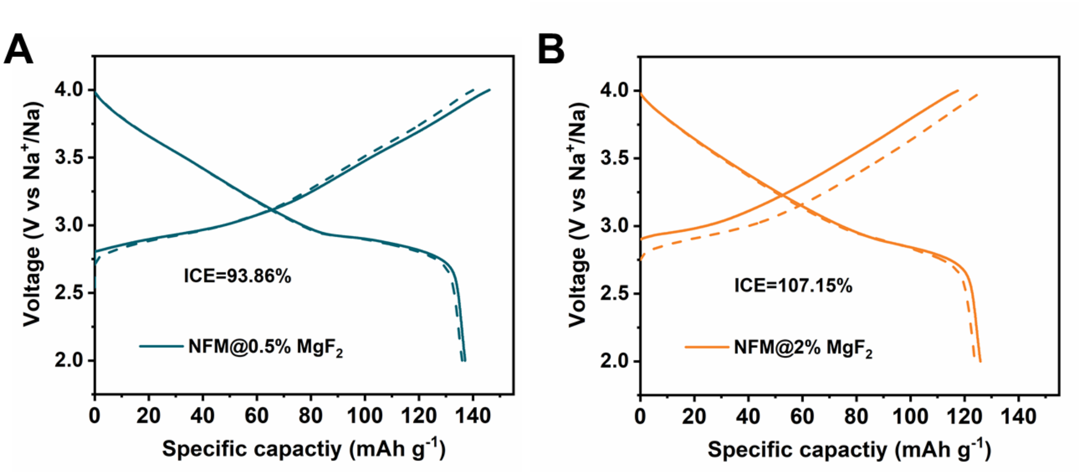
Supplementary Figure 1. NFM HAADF image and its corresponding EDS elemental picture of Na, Ni, Fe, Mn, and O.



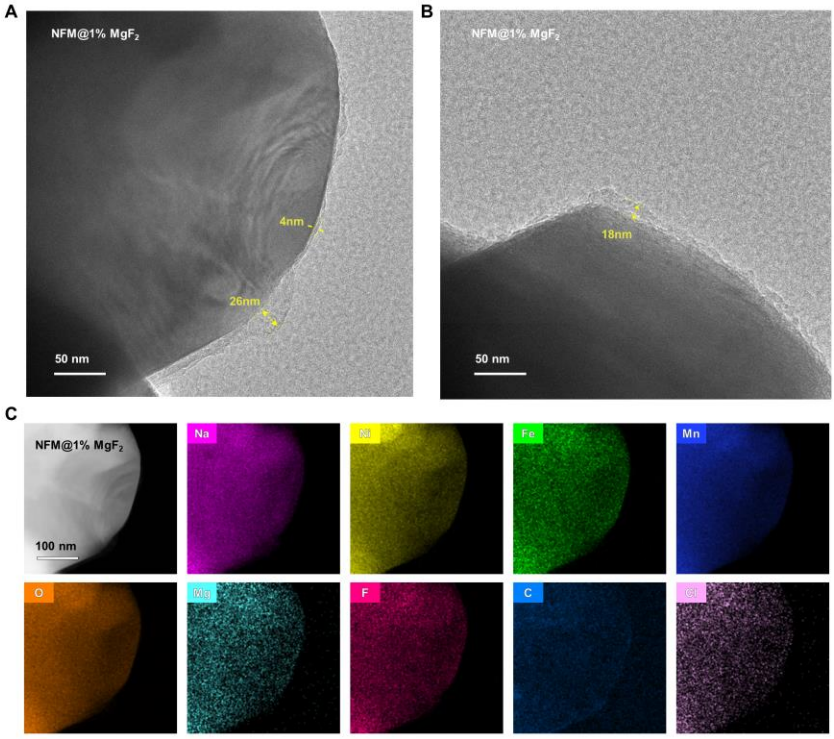
Supplementary Figure 2. (A, B) SEM images of the MgF_2 powder used for surface loading at different magnifications.



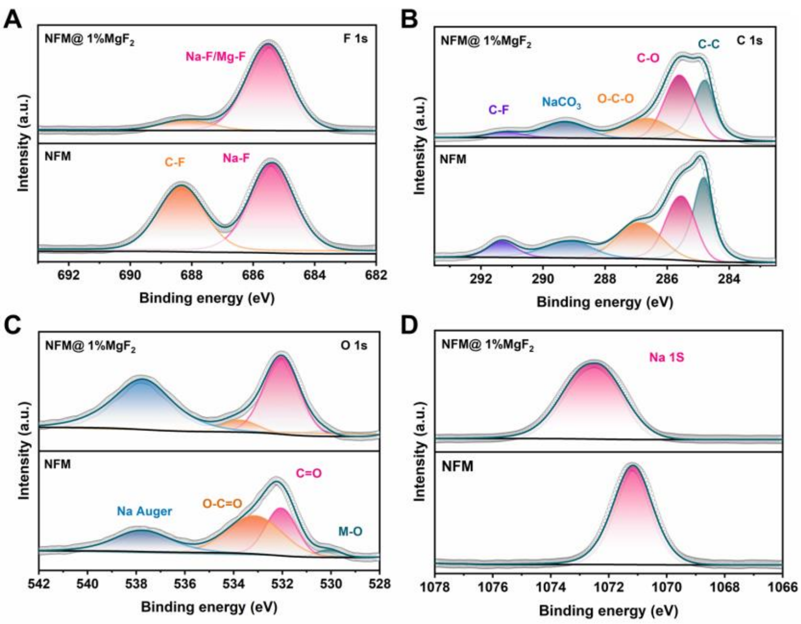
Supplementary Figure 3. XPS spectra of the elements of the NFM and NFM@1%MgF_2 samples



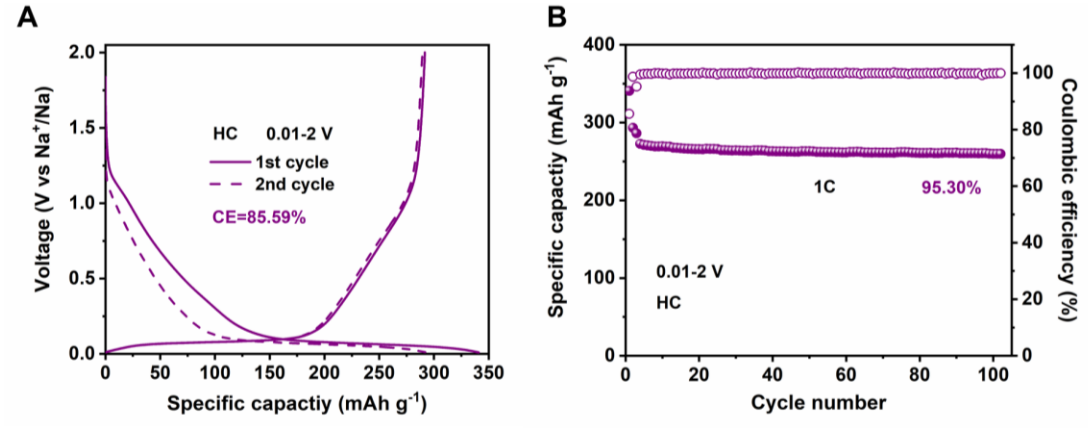
Supplementary Figure 4. (A) NFM@0.5%MgF_2 and (B) NFM@2%MgF_2 GCD curves for the first two cycles at 0.1C, the dashed line represents the second cycle.



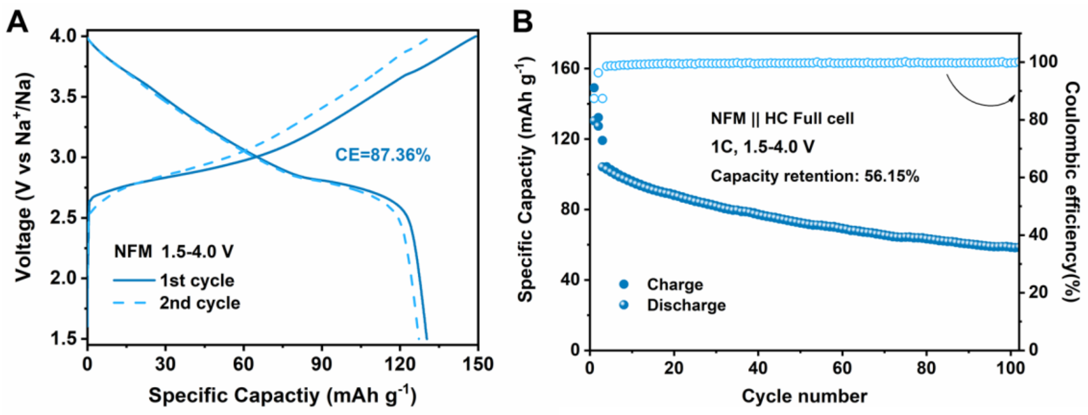
Supplementary Figure 5. (A, B) TEM images of the cycled NFM@1%MgF_2 collected from different regions. (C) HAADF-STEM image of the cycled NFM@1%MgF_2 and the corresponding elemental mapping results.



Supplementary Figure 6. High-resolution XPS spectra of cycled NFM and NFM@1%MgF_2. (A) F 1s, (B) C 1s, (C) O 1s, and (D) Na 1s.



Supplementary Figure 7. Electrochemical performance of HC in the 0.01-2 V voltage range. (A) GCD curves for the first two cycles at 0.1C, the dashed line represents the second cycle. (B) Cycling performance at 1C current density.



Supplementary Figure 8. (A) Capacity-voltage profiles of the NFM||HC full cell in the initial two cycles at 0.1 C in the voltage range of 1.5-4.0 V. The specific capacity is calculated based on the mass of cathode materials. (B) Cycling performance of the NFM||HC full cell at 1C for 100 cycles.

Supplementary Table 1. ICP-OES results of NFM and NFM samples loaded with MgF_2 samples Measured atomic ratio

Sample	Ni	Fe	Mn	Mg
NFM	0.3398	0.3343	0.3259	0
NFM@0.5%MgF_2	0.3385	0.3341	0.3274	0.0039
NFM@1%MgF_2	0.3373	0.3313	0.3314	0.0078

Supplementary Table 2. The comparison of electrochemical performance of NFM@1%MgF_2 with other modified NFM cathode materials

Samples	Voltage Window	Initial Coulombic Efficiency	Cycling Stability	Rate Capacity	Ref
$NaTi_2(PO_4)_3$ modified $NaNi_{1/3}Fe_{1/3}Mn_{1/3}O_2$	1.5–4.2 V	93.3%	77.5%, 100th, 1C	68.2 mAh g^{-1}, 10C	[1]
Na_2MoO_4-coated $NaNi_{1/3}Fe_{1/3}Mn_{1/3}O_2$	2.0–4.0 V	91.9%	62.9%, 100th, 1C	81.1 mAh g^{-1}, 10C	[2]
V dual-modification $NaNi_{1/3}Fe_{1/3}Mn_{1/3}O_2$	2.0–4.0 V	~94.3%	86.0%, 150th, 0.5C	85.8 mAh g^{-1}, 5C	[3]
0.5$NaPO_3$-coated $NaNi_{1/3}Fe_{1/3}Mn_{1/3}O_2$	2.0–4.0 V	~96.6%	80.1%, 150th, 1C	103.0 mAh g^{-1}, 10C	[4]
$NaNi_{1/3}Fe_{1/3}Mn_{1/3-0.02}Zr_{0.02}O_2$	2.0–4.0 V	~90.5%	77.7%, 300th, 1C	88.5 mAh g^{-1}, 10C	[5]
$NaCr_{0.95}Ni_{0.05}O_2$	2.0–3.6 V	97.7%	88.0%, 500th, 10C	91.2 mAh g^{-1}, 50C	[6]
$NaNi_{1/3}Fe_{1/3}Mn_{1/3}O_2$ @1%MgF2	2.0–4.0 V	100.9%	85.7%, 100th, 1C	82.1 mAh g^{-1}, 10C	This work

Supplementary Table 3. Simulated parameters from the EIS after different cycles of NFM and NFM@1%MgF_2 cathode

Sample	Cycle number	R_s (Ω)	R_{sf} (Ω)	R_{ct} (Ω)
NFM	2nd	6.345	0	1016
	100th	12.40	607.2	1305
NFM@1%MgF_2	2nd	5.252	0	191.1
	100th	11.60	540.8	969.8

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