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Supporting Information

2 **Self-Assembled Monolayer Boosts the Air-Stability and**
3 **Electrochemical Reversibility of O3-Type Layered Oxides for Sodium-**
4 **Ion Batteries**

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11 Experimental Section

12 1. Preparation of NFM and NFM@DHP

13 O₃-NaNi_{0.33}Fe_{0.33}Mn_{0.33}O₂ (NFM) powders were synthesized by a traditional sol-
14 gel route.^{1, 2} The stoichiometric amounts of CH₃COONa (5% excess),
15 Mn(CH₃COO)₂·4H₂O, Ni(CH₃COO)₂·4H₂O, and Fe(NO₃)₃·9H₂O were fully dissolved
16 in deionized water and then mixed with aqueous citric acid under vigorously stirred till
17 a clear solution was obtained. The resulting solution was heated and stirred in a 90 °C
18 oil bath, with excess aqueous solution evaporated off until a clear and viscous gel
19 formed. The as-formed gel was dried at 125 °C overnight to produce a loose and porous
20 precursor. Then, the precursor was ground, calcined in air at 500 °C for 6 h, reground,
21 pressed into pellets, and calcined again at 900 °C for 10 h. Finally, the pellets were
22 ground to obtain the final NFM powders.

23 The NFM@DHP composite was prepared using a straightforward infiltration
24 approach. An appropriate amount of dicetyl phosphate (C₃₂H₆₇O₄P) was fully dissolved
25 in 20 mL of tetrahydrofuran (THF) to form a 0.01 wt% solution. Then, 0.2 g of NFM
26 powders were immersed in the above solution. After vigorous stirring for 2 h at room
27 temperature, the dispersion was centrifuged, followed by thorough washing with THF
28 to remove residual DHP molecules. The precipitates were then vacuum-dried overnight
29 at 60 °C to give the target NFM@DHP composite.

30 To assess the air stability of NFM and NFM@DHP, the samples were exposed to
31 an environment with a relative humidity (RH) of 45-50% for various durations. This
32 was achieved by placing the materials on a watch glass in a sealed container with a
33 saturated solution of K₂CO₃. The container was placed in a controlled environment at
34 30°C, with the RH regulated at 45-50% using a hygrometer. According to the
35 experimental requirements, the materials were placed for certain days to obtain the
36 target materials.

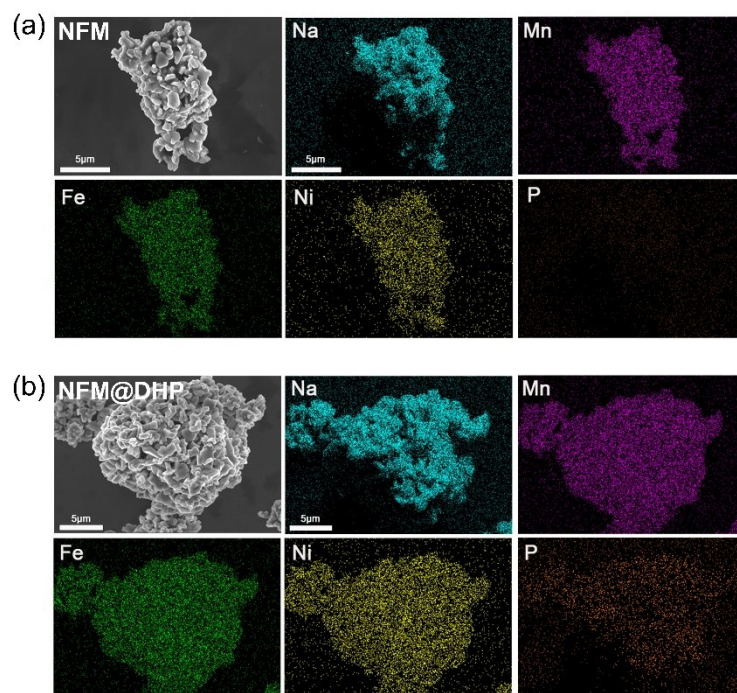
37 2. Characterizations.

38 The crystalline structures of the samples were identified using X-ray diffraction
39 (XRD, Bruker D8 ADVANCE) with Cu K α radiation. The GSAS-II software was used
40 to obtain the Rietveld refinement data. The morphologies of the samples were observed
41 by scanning electron microscopy (SEM, TESCAN MIRA3) equipped with energy-
42 dispersive X-ray spectroscopy (EDS). Transmission electron microscopy (TEM, Talos
43 f200i) was manipulated to acquire images of the refined structures of the samples.

44 Fourier transform infrared spectroscopy (FT-IR, BRUKER TENSOR II (FTS6000))
45 was recorded using KBr pellets in a unit of cm^{-1} . The chemical compositions were
46 detected on an X-ray photoelectron spectrometer (XPS, Thermo Fischer, ESCALAB
47 Xi+) under a vacuum of 8×10^{-10} Pa (the C 1s peak at 284.8 eV as reference). Contact
48 angle analysis was recorded on a SINDIN SDC-200S instrument at room temperature.

49 ***3. Electrochemical measurements.***

50 The electrochemical performance of the samples was evaluated using CR2032
51 coin-type cells assembled in an argon-filled glove box. The cathodes were prepared by
52 mixing the active materials with super-P carbon black and polyvinylidene fluoride
53 (PVDF) binder with a mass ratio of 8:1:1 in N-methyl pyrrolidone (NMP) to obtain a
54 stable homogeneous suspension, which was then coated on aluminum foil. The mass
55 loading of the active material on the electrode was 1-1.5 mg cm^{-1} . Prior to slurry
56 preparation, all exposed samples were dried under vacuum conditions at 80 °C. Sodium
57 metal foil was used as then anode and glass fiber (GF/D, Whatman, Φ 19 mm) was used
58 as the separator. The electrolyte was 1 M NaClO_4 in a mixture of propylene
59 carbonate/ethylene carbonate (PC/EC = 1:1 in volume) with fluoroethylene carbonate
60 (5% volume), with about 100 μL of electrolyte added into each coin-type cell using a
61 pipette. All batteries were rested overnight before testing. The cells were initially
62 activated for 3 cycles at 0.1 C before undergoing long-cycle testing. The cycled
63 cathodes (NFM and NFM@DHP) for XRD measurement were rinsed three times with
64 propene carbonate and subsequently blow-dried under argon gas. Electrochemical
65 impedance spectra (EIS) were acquired by an Admiral Instruments electrochemical
66 workstation. Charge and discharge measurements were carried out using multichannel
67 battery testing systems (CT2001A Wuhan LAND Electronics Co., Ltd., China) at room
68 temperature.



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70 **Figure S1** EDS mappings for Na, Mn, Fe, Ni, and P elements of a) NFM and b) NFM@DHP.

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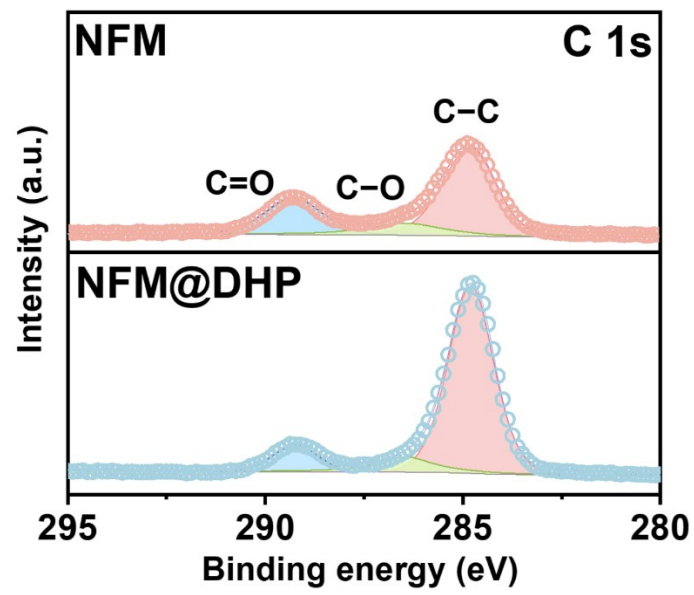
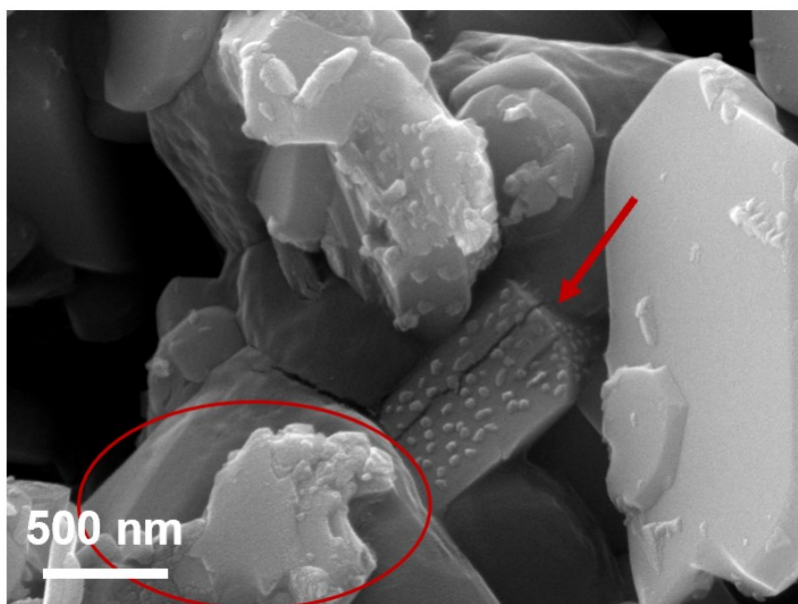


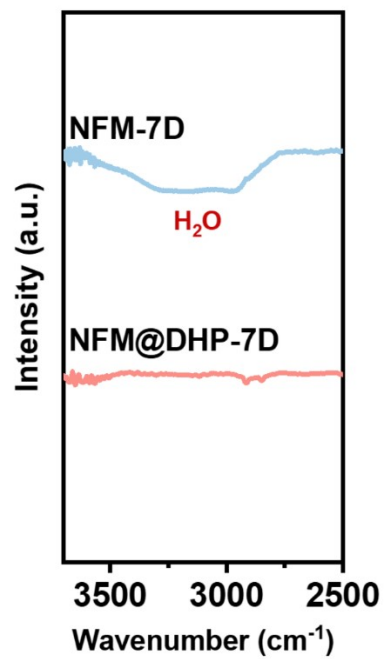
Figure S2 C 1s XPS spectra of NFM and NFM@DHP.

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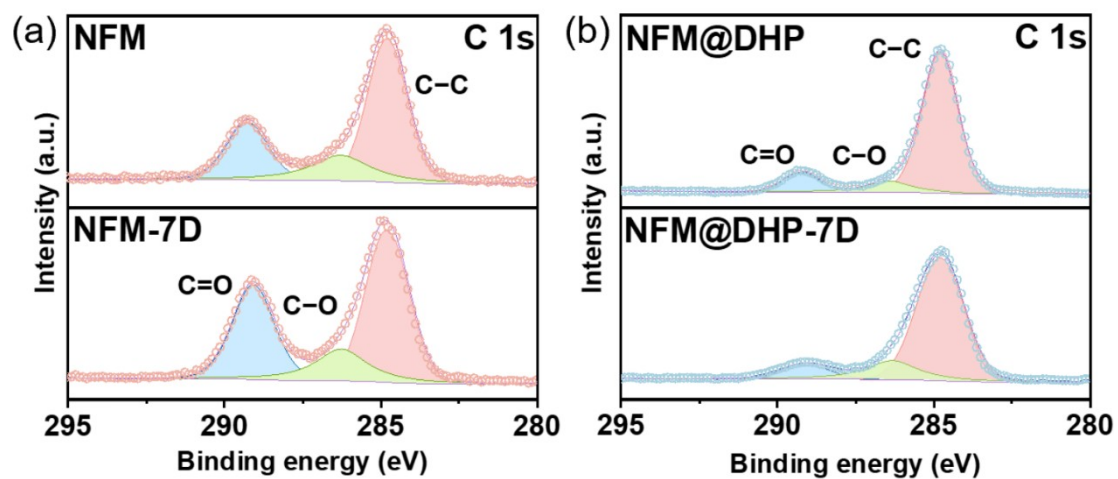
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Figure S3 SEM image of NFM-7D.



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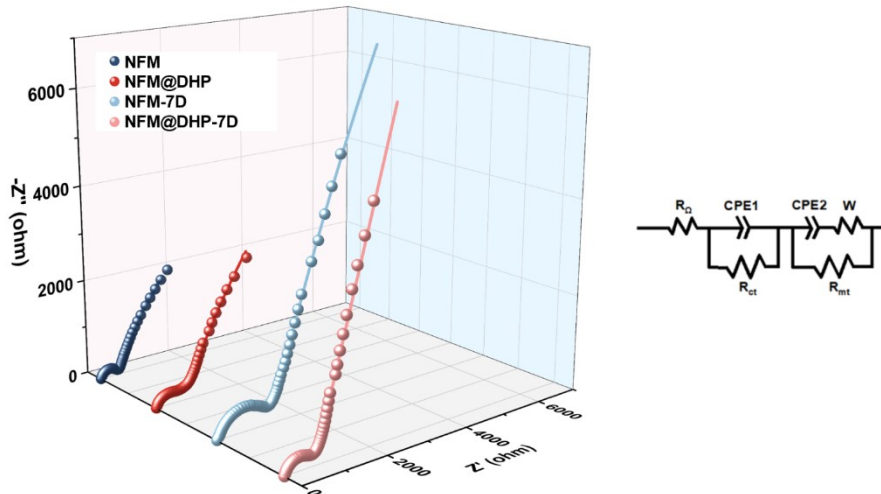
Figure S4 FTIR spectra of NFM-7D and NFM@DHP-7D.



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82 **Figure S5** C 1 s XPS spectra of a) NFM and NFM-7D, and b) NFM@DHP and NFM@DHP-7D.

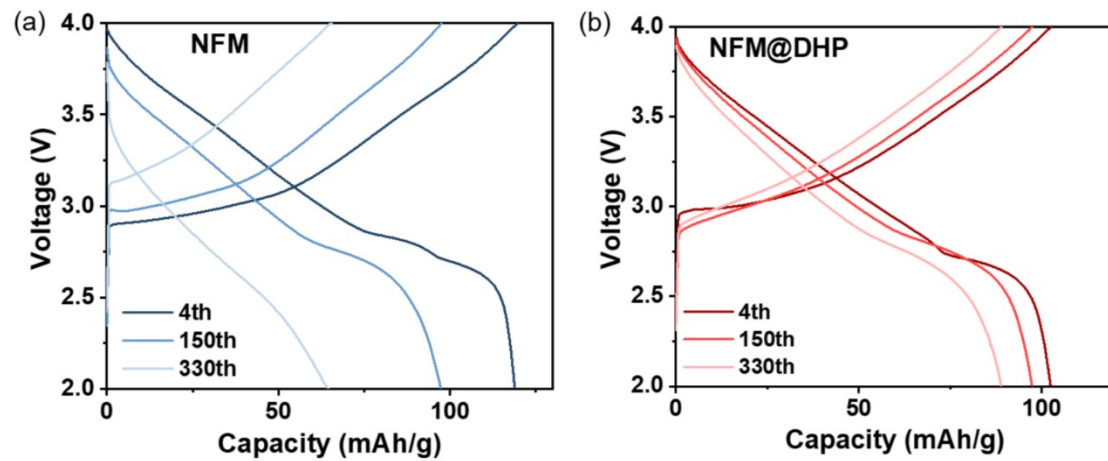
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85 **Figure S6** Nyquist plots of NFM and NFM@DHP before and after being exposed for 7 days. The
 86 increased interfacial resistance of NFM@DHP should be ascribed to the presence of the DHP
 87 coating on the electrode surface.

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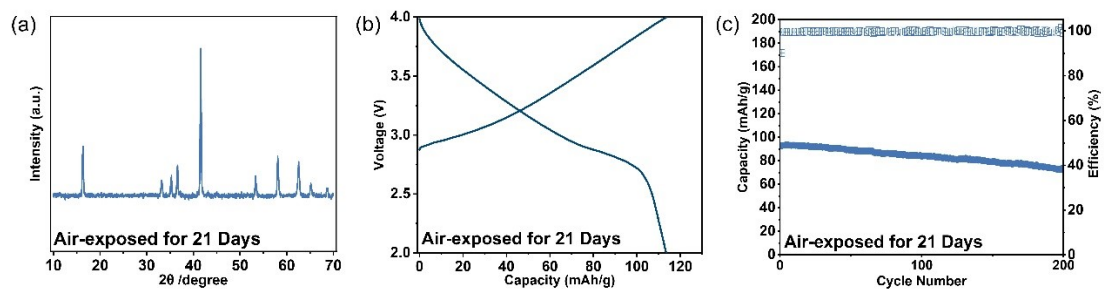
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91 **Figure S7** Charge/discharge curves of a) NFM and b) NFM@DHP at the 4th, 150th, and 330th

92 cycles.

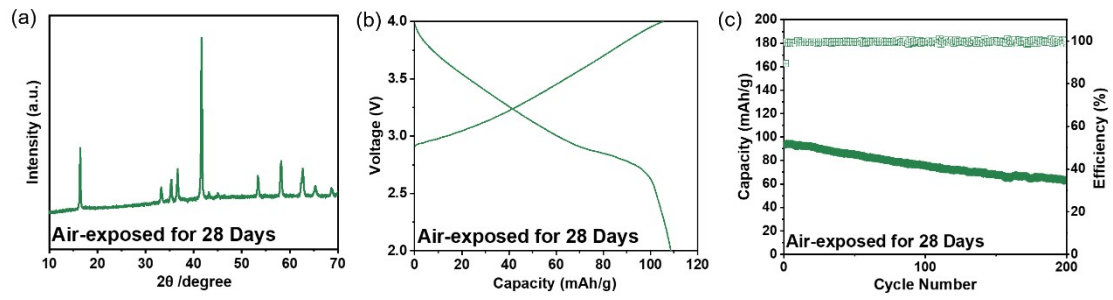
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95 **Figure S8** a) XRD spectrum, b) the first charge/discharge curve at 0.1C, and c) cycling stability at
96 1C of NFM@DHP after 21-days of air exposure.

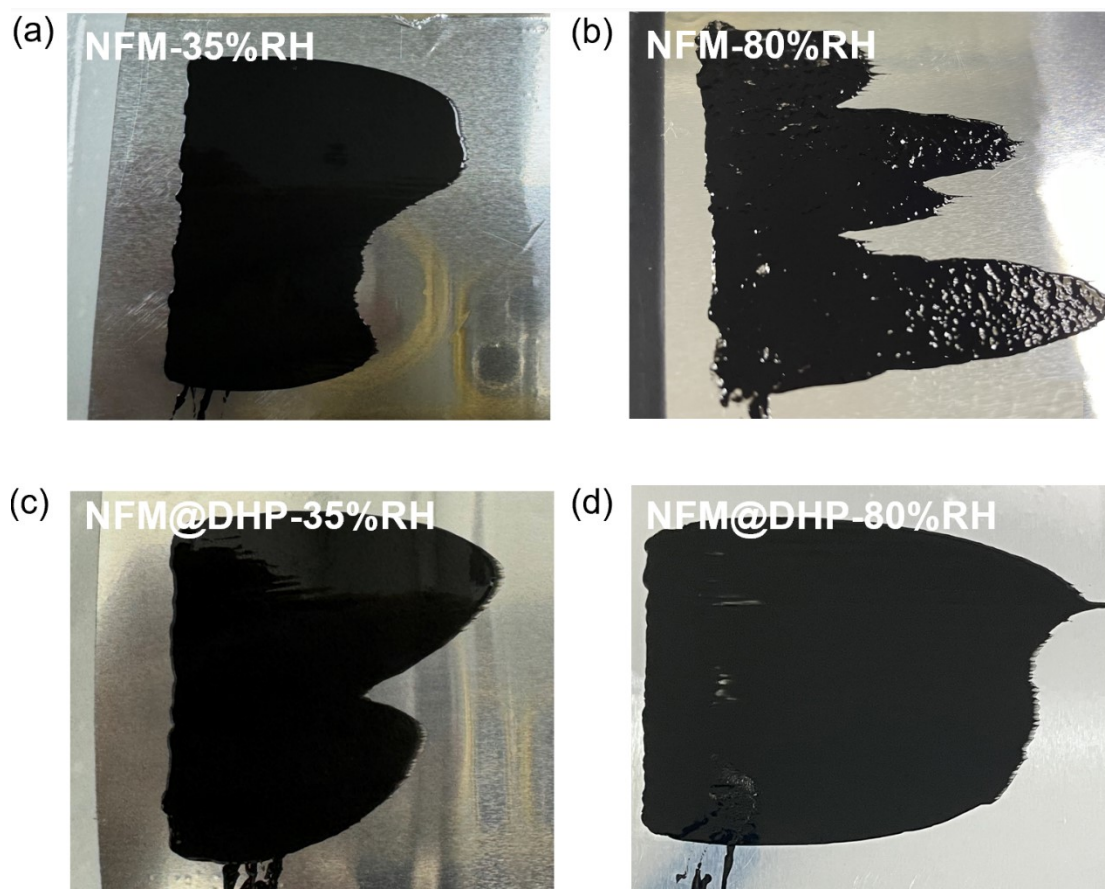
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99 **Figure S9** a) XRD spectrum, b) the first charge/discharge curve at 0.1C, and c) cycling stability at
100 1C of NFM@DHP after 28-days of air exposure.

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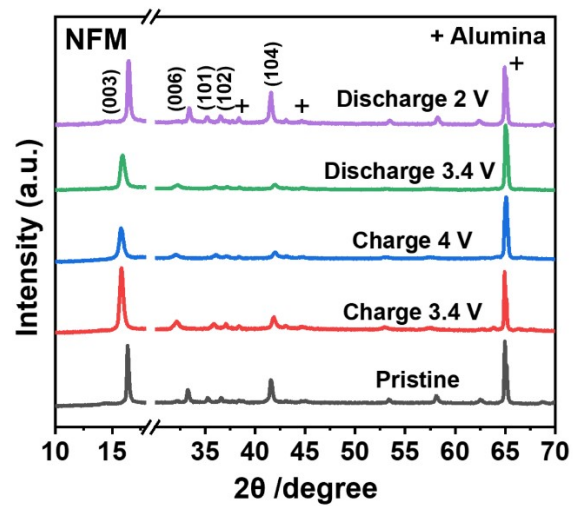


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103 **Figure S10** Photographs of the slurries of a, b) NFM and c, d) NFM@DHP under a, c) humid and
104 b,d) dry air.

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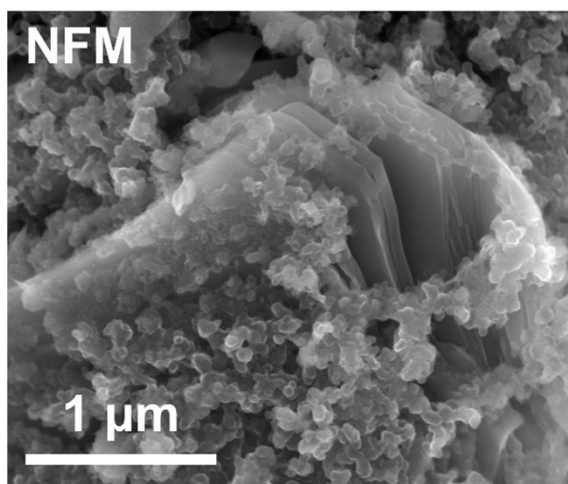
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Figure S11 Ex-situ XRD of the NFM electrode during the initial cycle at 0.1 C.



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Figure S12 SEM image of NFM after 200 cycles at 1C.

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