

Supporting Information

Construction of Uniform MgO Nanoshells for Improved High-Voltage Performance of Li-Ion Battery

Experimental Section

Sample Preparation.

All chemicals used in this study were of analytical grade and procured from Sinopharm Chemical Reagent Co., Ltd. They were utilized as received without any further purification. Milli-Q water (resistivity > 18 MΩ) was employed for all experimental procedures.

Preparation of Silicon dioxide (SiO₂) nanoparticles with Mg (OH)₂ coating.

The SiO₂ nanoparticles were prepared using the classical Stöber method.¹ Specifically, 1 mL tetraethyl orthosilicate (TEOS), 2 mL deionized water and 3 mL ammonia solution (28 wt%) were added into 150 mL ethanol and allowed to react for 24 h at room temperature.

The SiO₂@Mg(OH)₂ sample was synthesized with a wet chemistry process, 90 mg magnesium acetate tetrahydrate (Mg(CH₃COO)₂·4H₂O), 64 mg urea, and 32 mg hexamethylenetetramine (HMTA) were dissolved in 30 mL of deionized water. Subsequently, 15 mg SiO₂ was dispersed into this buffer solution via ultrasound treatment. The mixture was continuously stirred at 80 °C for 5 h. The final product was collected through washing and centrifugation cycles and dried at 80 °C for 12 h. The thickness of the Mg (OH)₂ shell could be adjusted by varying the amounts of SiO₂ used in the synthesis process.

Preparation of lithium-rich manganese-based cathode material coating with Mg (OH)₂ (R-Li-Mn@Mg (OH)₂).

The lithium-rich manganese-based cathode material (R-Li-Mn) was purchased from Ningbo Gauss New Energy Technology Co. For preparing R-Li-Mn@Mg (OH)₂ nanoparticles, 90 mg Mg(CH₃COO)₂ · 4H₂O, 64 mg urea and 32 mg HMTA were dissolved in 30 mL deionized water, followed by the dispersion of 500 mg pristine R-Li-Mn powders in it. The mixture was stirred at 80°C. After 5 h, the products were collected by centrifugation and dried at 80 °C.

Synthesis of pristine LiNi_{0.5}Mn_{1.5}O₄ (LNMO-P) materials.

The pristine LNMO cathode material was synthesized with a sol-gel process. Specifically, lithium acetate, nickel acetate, and manganese acetate were dissolved in deionized water with a molar ratio of 1.03:0.5:1.5. Glycolic acid was added into this solution as a chelating agent. The pH of the solution was tuned to 8.5–9.0 using ammonium hydroxide. After the evaporation at 80 °C, the resulting gel was sintered at 900°C in atmosphere for 10 h.

Preparation of LiNi_{0.5}Mn_{1.5}O₄ materials coating with Mg (OH)₂ (LNMO@ Mg (OH)₂) and MgO (LNMO-Mg).

90 mg Mg (CH₃COO)₂ · 4H₂O, 64 mg urea and 32 mg HMTA were dissolved in 30 mL deionized water, followed by the dispersion of 1 g pristine LNMO powders in it. The mixture was stirred at 80°C. After 5 h, the products were collected by centrifugation and dried at 80 °C to obtain the sample of LNMO@5nm Mg (OH)₂. The LNMO-Mg sample was prepared by calcining the sample of LNMO@5nm Mg (OH)₂ at 650 °C for 2 h. The thickness of Mg(OH)₂ shell can be adjusted by changing the amount of LNMO powder in the synthesis process. The samples with different Mg(OH)₂ coating thicknesses (2 nm and 10 nm) were sintered at 650°C for 2h to obtain samples with different MgO coating thicknesses (LNMO@2 nm Mg(OH)₂-650°C and LNMO@10 nm Mg(OH)₂-650 °C).

Material Characterization.

Transmission electron microscopy (TEM), high-resolution TEM (HRTEM), and energy-dispersive spectroscopy (EDS) elemental mapping in dark-field mode were captured using a JEOL 2100F instrument at an operating voltage of 200 kV. X-ray diffraction (XRD) patterns were generated utilizing a Bruker D8 Advance diffractometer with Cu Kα radiation (λ = 1.5418 Å). X-ray photoelectron spectroscopy (XPS)

measurements were performed on a Kratos Axis Supra using Al K α radiation, with binding energies calibrated relative to the hydrocarbon C 1s peak at 284.8 eV.

Electrochemical Tests.

Electrochemical measurements were tested with CR2032 coin cells assembled in an argon-filled glovebox using lithium metal as the counter and reference electrodes. The cathodes were prepared by mixing the active materials, acetylene black (Super-p), and poly(vinyl difluoride) (PVDF, Aldrich) at a weight ratio of 8:1:1, pasting on a pure Al foil (99%, Goodfellow), and cutting into circular electrodes with diameter of 1.0 cm. Polypropylene membrane (Celgard) was used as a separator. The electrolyte, 1 M LiPF₆ in ethylene carbonate (EC)/dimethyl carbonate (DMC)/diethyl carbonate (DEC) (1:1:1, in vol %), was purchased from Kishida Chemical Co., Ltd. Galvanostatic tests of the assembled cells were performed with a Land CT2001A battery test system between 3.0 and 5.0 V. The electrochemical impedance spectroscopy (EIS) was tested on an electrochemical workstation (Auto Lab, PGSTA302N).

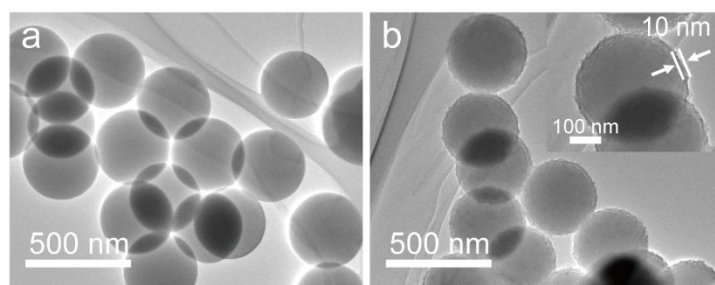


Figure S1. TEM image of SiO₂ nanospheres (a) and SiO₂ nanospheres coated with 10 nm magnesium species (b).

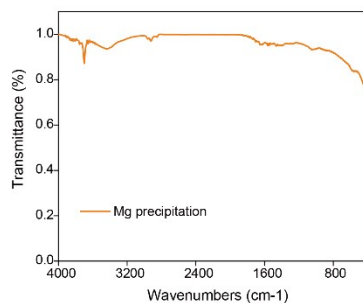


Figure S2. Fourier transform infrared spectroscopy (FTIR) spectra of Mg precipitation. The pronounced and intense peak observed at 3697 cm⁻¹ is attributed to the OH group present in magnesium precipitation, while the strong peak around 440 cm⁻¹ corresponds to the Mg–O stretching vibration. The bands within the range of 1440–1650 cm⁻¹ are associated with the –OH stretching mode in water. Additionally, a broad band at 3440 cm⁻¹ is ascribed to surface-adsorbed –OH groups.²

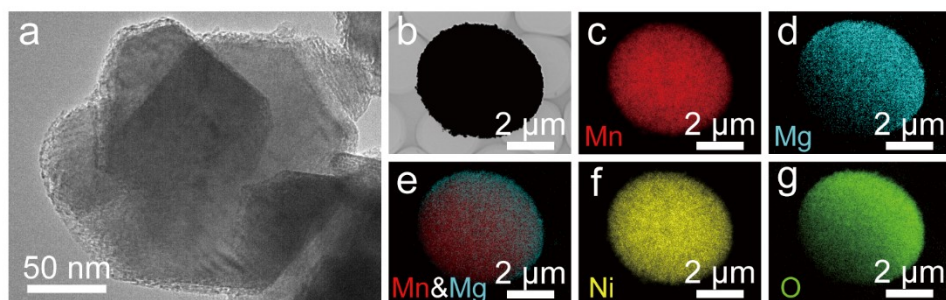


Figure S3. TEM images (a) and corresponding EDS spectra (b-g) of lithium-rich manganese-based cathode particles coated with $\text{Mg}(\text{OH})_2$ nanolayer.

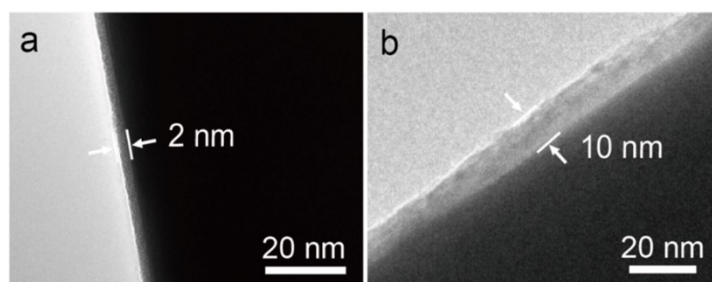


Figure S4. TEM images of LNMO coated with different thicknesses of $\text{Mg}(\text{OH})_2$: (a) 2 nm and (b) 10 nm.

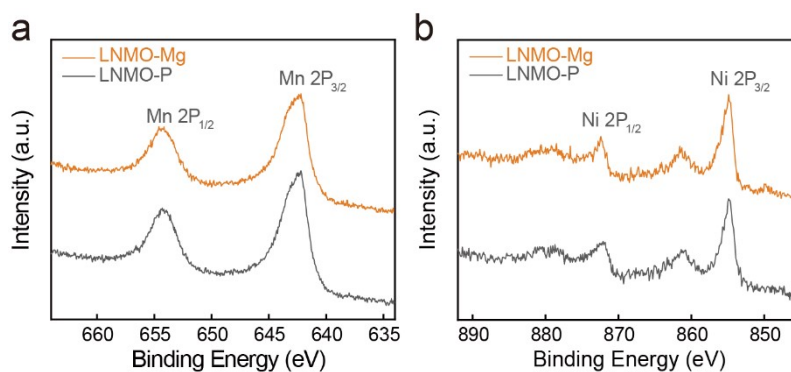


Figure S5. The Mn 2p (a) and Ni 2p (b) XPS peaks of LNMO-Mg and LNMO-P.

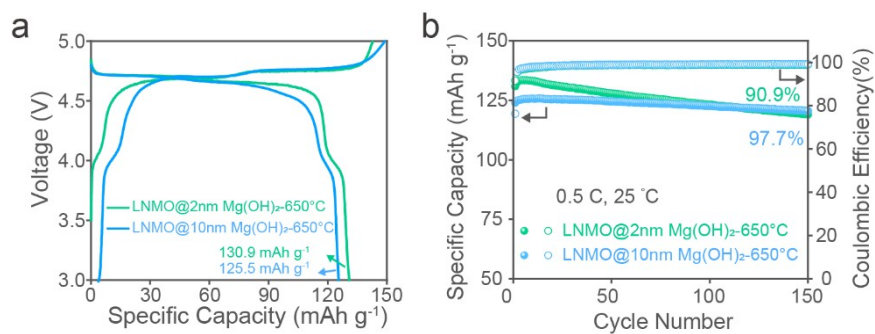


Figure S6. Charge and discharge profiles for the first cycle (a) and cycling performance (b) of LNMO@2 nm $\text{Mg}(\text{OH})_2$ -650°C and LNMO@10 nm $\text{Mg}(\text{OH})_2$ -650°C button half-cells at 0.5 C for 150 cycles.

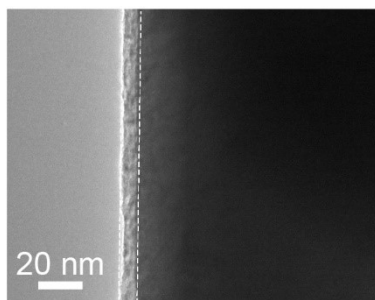


Figure S7. HRTEM of LNMO-Mg after 150 cycles at 0.5 C.

Table S1. The EIS fitting results for LNMO-P and LNMO-Mg samples before and after cycling.

Sample	Re(Ω)	Rct(Ω)
LNMO-P (before cycling)	2.0	123.2
LNMO-Mg (before cycling)	2.0	58.1
LNMO-P (after cycling)	3.9	276.9
LNMO-Mg (after cycling)	3.4	146.1

References

1. W. Stöber, A. Fink, E. J. J. o. c. Bohn and i. science, 1968, **26**, 62-69.
2. D. An, X. Ding, Z. Wang and Y. Liu, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 2010, **356**, 28-31.