

Supporting Information

Construction of Li_3PO_4 nanoshells for improved electrochemical performance of Ni-rich Cathode material

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Experimental sections

Preparation of $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$. The cathode materials of $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ (622) were prepared through a coprecipitation process by following the literature.^[1] Typically, 1 mol L^{-1} transition metal salt ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$, and $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ with a molar ratio of 0.6:0.2:0.2), 1 mol/L NaOH and moderate amounts of NH_4OH were mixed in 500 rpm. After 12 h, the products ($\text{Ni}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}(\text{OH})_2$) were collected and washed by water and ethanol. Then, we put the product in vacuum drying oven for 12 h at $70\text{ }^\circ\text{C}$. The dried materials were mixed with Li_2CO_3 in a molar ratio of 1:0.6. Finally, the mixture was annealed at $750\text{ }^\circ\text{C}$ for 18 h in oxygen atmosphere to obtain 622.

Preparation of 622@PZM. 0.3 g 4,4'-Oxydianiline (ODA) and 0.15 g Hexachlorocyclotriphosphazene (HCCP) were dissolved in 30 ml acetonitrile. Then, 5 g 622 and 0.5 ml triethylamine (TEA) were added to the mixture under vigorously stirring. After 12 h, the 622@PZM was collected and washed with ethanol through centrifugation. Finally, the obtained products were put in vacuum drying oven at $80\text{ }^\circ\text{C}$ for 5 h.

Preparation of electrode materials. The obtained 622@PZM was heated at $700\text{ }^\circ\text{C}$ in O_2 atmosphere for 2 h to form Li_3PO_4 coating layers on the surface of 622, which was referred as 622@LPO.

Characterization. We utilized a field-emission scanning electron microscope (SEM, JEOL 6701F, Japan) and a transmission electron microscope (TEM, JEOL-2100F,

Japan) with energy dispersive spectroscopy (EDS) mapping to detect the morphology and the element distribution of samples. A Bruker D8 Advance diffractometer (Germany) with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) was utilized to record the crystal structure of samples. X-ray photoelectron spectroscopy (XPS) was utilized to detect the surface chemical state. BRUKER IR microscope (SENSOR-27) was utilized to collect FT-IR spectra. Focused ion beam (FIB) and SEM was used to observe the cross section of sample. Reference to the Feng Wu's work, we measured the pH value of the sample. The detailed procedures were shown below: Mixing 10.0 g materials and 100 ml deionized water under vigorously stirring for 5 h, and allowing the mixture to stand for 0.5 h, then utilizing the pH detectors (Mettler Toledo) to measure the pH value of samples.

CR2032 coin cells were utilized to test the electrochemical performance of samples. To prepare the cathode, we mixed the active materials with carbon black (super-p) and poly(vinyl difluoride) (PVDF, Aldrich) with a weight ratio of 8:1:1, and disperse the mixture on a Al foil (99%, Aldrich). After dried in vacuum oven, the coating foils were cut into wafers with a diameter of 12 mm, which were used as cathodes in the battery. Lithium foil was utilized as anode, 1 M LiPF₆ dissolving in ethylene carbonate (EC)/dimethyl carbonate (DMC)/diethyl carbonate (DEC) (1:1:1, in vol %) was utilized as electrolyte, polypropylene membrane (Celgard) was used as a separator. The process of assembling coin battery was conducted in argon-filled glove box. A Land-CT2001A system was utilized to test the galvanostatic charge-discharge performance between 3.0-4.5 V (vs Li⁺/Li). Autolab PGSTAT 302N (Metrohm, Switzerland) was used to record the Electrochemical impedance spectroscopy (EIS) with the frequency from 100 kHz to 0.1 Hz.

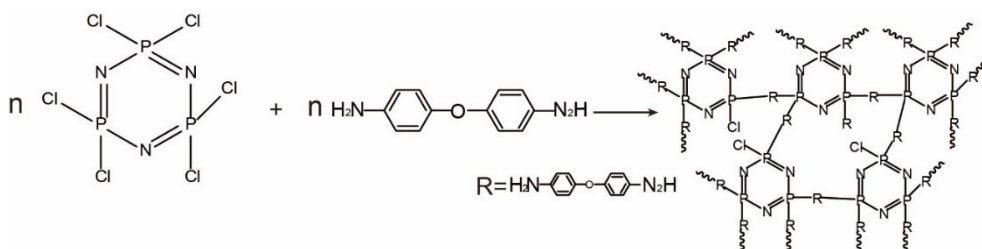


Fig. S1. The chemical reaction equation of forming polyphosphazene.

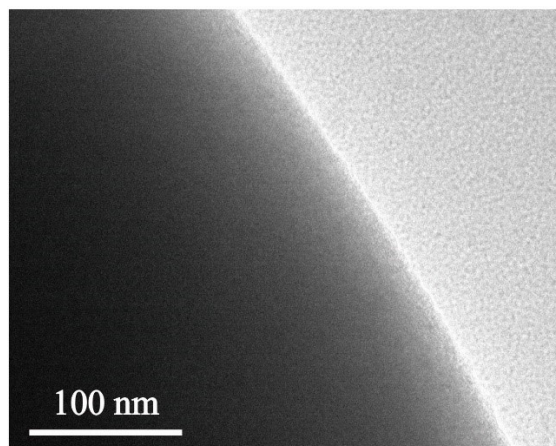


Fig. S2. TEM image of pristine 622

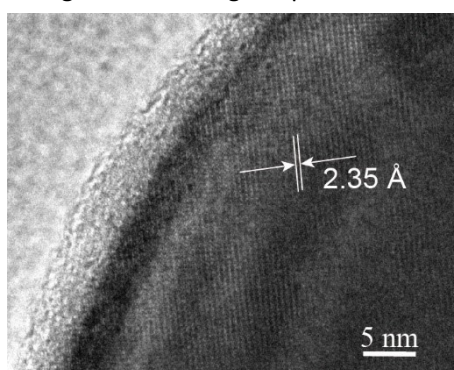


Fig. S3. HRTEM image of 622@PZM.

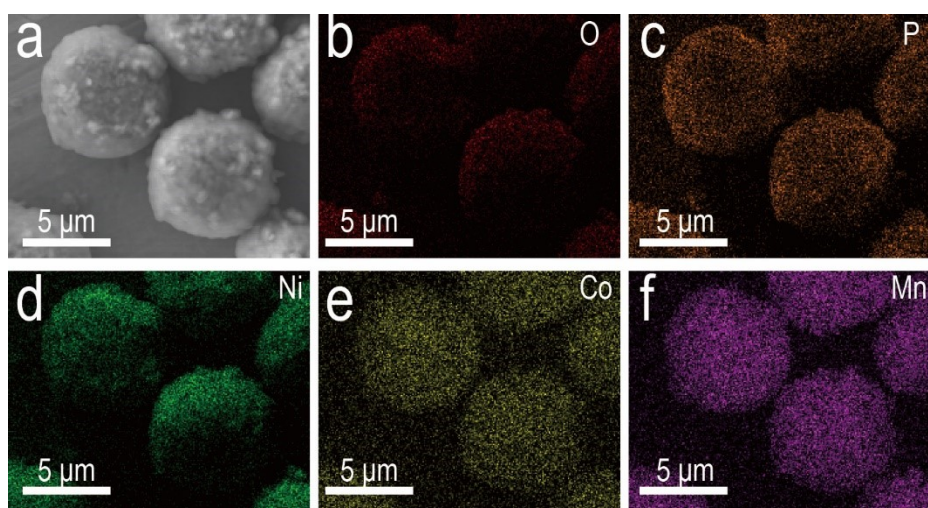


Fig. S4. The elemental mapping of 622@PZM

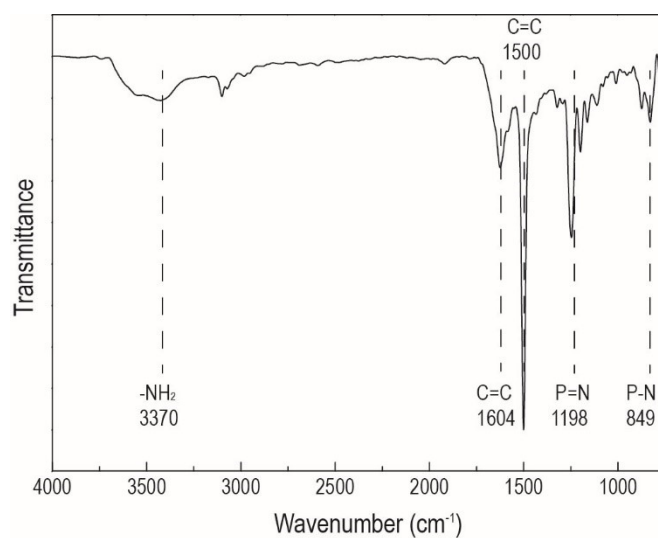


Fig. S5. FT-IR spectra of nanoshells

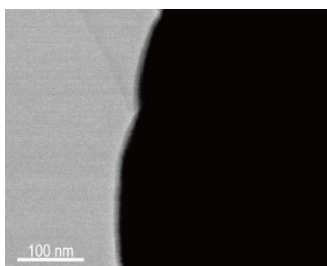


Fig. S6. A TEM image of the surface structure of a randomly picked 622@LPO particle.

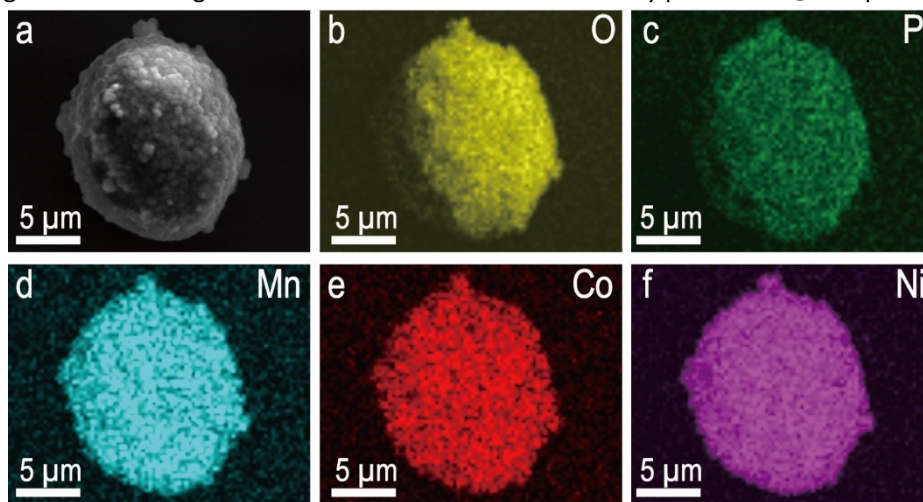


Fig. S7 The elemental mapping of 622@LPO

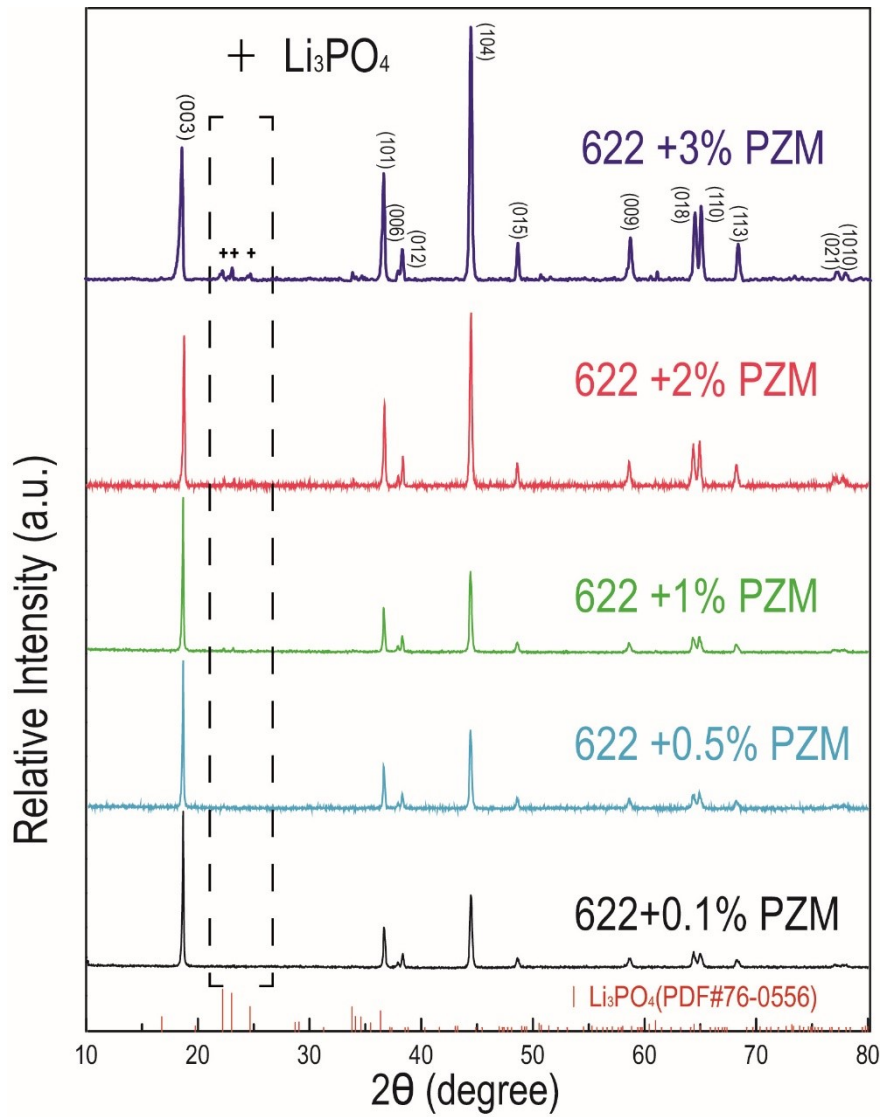


Fig. S8. XRD patterns of the control samples heated at 700 °C in an O₂ atmosphere for 2h. Different PZM contents were used to reveal the impact of their amounts on the materials formed in the product. The emerging of tiny Li₃PO₄ peaks was marked by + along with the increase of PZM contents.

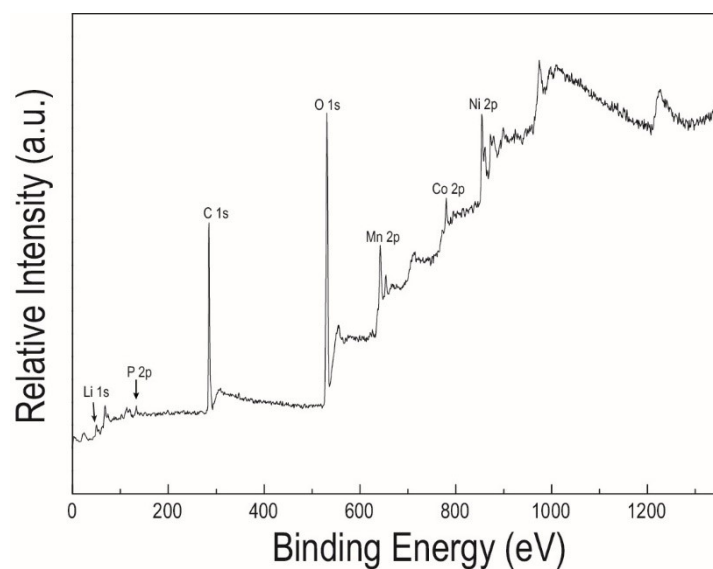


Fig. S9. XPS survey spectrum of PZM@LPO

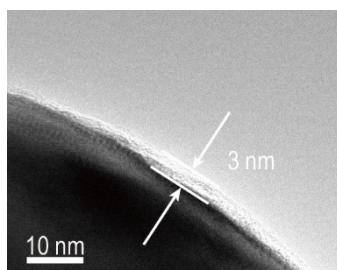


Fig. S10. A representative TEM image of the surface structure of the 622@LPO product.

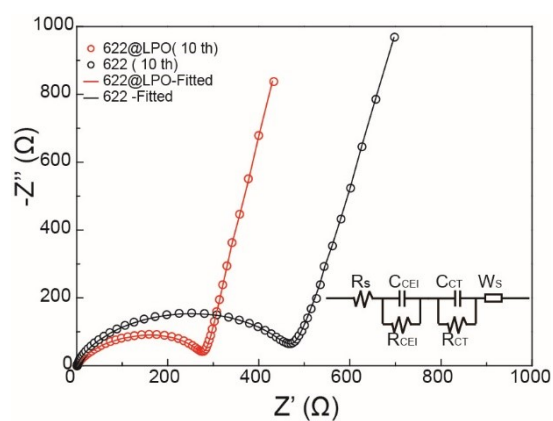


Fig. S11. Electrochemical impedance spectroscopy of 622 and 622@LPO at different cycles.

Table. S1. Atomic coordinates for 622@LPO

Space group : R-3m				
$a_{\text{hex}}:2.8717\text{Å}$	$c_{\text{hex}}:14.2307\text{ Å}$		Volume:101.63577 Å^3	$S(R_{\text{wp}}/R_{\text{exp}})=1.196$
Atom	x	y	z	Occupancy
Li(Li)	0	0	0.5	0.9648

Ni(Ni)	0	0	0	0.5648
Co	0	0	0	0.2
Mn	0	0	0	0.2
O	0	0	0.2417	1
Li(Ni)	0	0	0	0.0352
Ni(Li)	0	0	0.5	0.0352

Table. S2. Atomic coordinates for 622

Space group : R-3m				
a_{hex} :2.8708Å	c_{hex} :14.2284 Å		Volume:101.55790 Å ³	$S(R_{\text{wp}}/R_{\text{exp}})=1.153$
Atom	x	y	z	Occupancy
Li(Li)	0	0	0.5	0.9643
Ni(Ni)	0	0	0	0.5643
Co	0	0	0	0.2
Mn	0	0	0	0.2
O	0	0	0.2417	1
Li(Ni)	0	0	0	0.0357
Ni(Li)	0	0	0.5	0.0357

Table.S3 Fitted results of EIS spectra.

Impedance	$R_{\text{CEI}} (\Omega)$	$R_{\text{CT}}(\Omega)$
622	32.2	126.7
622@LPO	24.6	133.2
622 (10 th)	75.2	486.3
622@LPO (10 th)	37.3	263.4
622 (100 th)	194.6	762.5
622@LPO (100 th)	58.9	438.1

Notes and references

1 H. Kim, M. G. Kim, H. Y. Jeong, H. Nam and J. Cho, Nano Letters, 2015, 15, 2111–2119.