

Supplementary information

Construction of Uniform Transition-metal Phosphate Nanoshells and Its Potential for high performance Li-ion Battery Performance

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Experimental section

Chemicals

NiSO₄·6H₂O, CoSO₄·7H₂O, MnSO₄·H₂O, urea, hydrochloric acid, ethanol, N-Methyl pyrrolidone, N, N-dimethylformamide, ethylene glycol and tetraethylene glycol were all of analytical purity and purchased from Sinopharm Chemical Reagent Co., Ltd. NH₄H₂PO₄ was purchased from Alfa Aesar. SnO₂ nanoparticles (~50 nm), silicon nanoparticles (~80 nm), multi-walled carbon nanotubes (MWCNT) were purchased from Beijing DK nano technology Co.,Ltd. All chemicals were purchased and used as received without further purification. Deionized water (resistance > 18 MΩ) produced by Milli-Q was used for all experiments. The polystyrene nanospheres (PS), 3-aminophenol formaldehyde nanospheres (3-AF), and the pristine LiNi_{0.5}Mn_{1.5}O₄ (LNMO) were synthesized following the literature procedure¹⁻³.

Sample preparation

Preparation of PS@Ni₃(PO₄)₂ core-shell composites: 0.041g of PS microspheres powders were dispersed in a light green mixture solvent of H₂O and ethylene glycol (H₂O: ethylene glycol=1:5, v/v) containing 0.046 mmol NiSO₄·6H₂O and 0.104 mmol NH₄H₂PO₄. Then 0.52 g urea was added to the above mixture under continuously stirring. The mixture was heated at 80 °C for 2 h under continuously magnetic stirring after adjusting the pH of the turbid solution above to 4.0 by hydrochloric acid. The obtain sample was filtered, washed with distilled water and absolute ethyl alcohol, then dried at 80 °C for 8 h. In addition, The thickness of Ni₃(PO₄)₂ shells could be tuned simply by adjusting the concentration of NiSO₄·6H₂O in the range of 0.02 ~ 0.5 mmol, the addition of NH₄H₂PO₄ from 0.05 to 1.0 mmol.

Preparation of hollow $Ni_3(PO_4)_2$ nanospheres: Making the prepared PS@ $Ni_3(PO_4)_2$ core-shell composites above heated at 500 °C for 2 h to remove the core material of PS nanospheres, then the uniform hollow $Ni_3(PO_4)_2$ nanospheres could be obtained.

Preparation of 3-AF@ $Ni_3(PO_4)_2$: 0.038 g 3-AF nanospheres, 0.046 mmol $NiSO_4 \cdot 6H_2O$, 0.104 mmol $NH_4H_2PO_4$ and 0.55g $CO(NH_2)_2$ were slowly added in the mixture solvent of H_2O and ethylene glycol (H_2O : ethylene glycol=1:5, v/v) under mechanical magnetic stirring. Subsequently, the resultant solution was titrated to pH ~ 4.0 by hydrochloric acid and then incubated at 80 °C for 2h under continuously magnetic stirring. The obtain sample was filtered, washed with distilled water and absolute ethyl alcohol, then dried at 80 °C for 8 h, respectively.

Preparation of SnO_2 @ $Ni_3(PO_4)_2$: 0.10g SnO_2 nanoparticles, 0.035 mmol $NiSO_4 \cdot 6H_2O$, 0.086 mmol $NH_4H_2PO_4$ and 0.63g $CO(NH_2)_2$ were slowly added in the mixture solvent of H_2O and ethylene glycol (H_2O : ethylene glycol=1:5, v/v) under mechanical magnetic stirring. Subsequently, the resultant solution was titrated to pH ~ 4.0 by hydrochloric acid and then incubated at 80 °C for 2h under continuously magnetic stirring. The obtain sample was filtered, washed with distilled water and absolute ethyl alcohol, then dried at 80 °C for 8 h, respectively.

Preparation of Si@ $Ni_3(PO_4)_2$: 0.015 g Si nanoparticles, 0.015 mmol $NiSO_4 \cdot 6H_2O$, 0.032 mmol $NH_4H_2PO_4$ and 0.53 g $CO(NH_2)_2$ were slowly added in the mixture solvent of H_2O and ethylene glycol (H_2O : ethylene glycol=1:5, v/v) under mechanical magnetic stirring. Subsequently, the resultant solution was titrated to pH ~ 4.0 by hydrochloric acid and then incubated at 80 °C for 2h under continuously magnetic stirring. The obtain sample was filtered, washed with distilled water and absolute ethyl alcohol, then dried at 80 °C for 8 h, respectively.

Preparation of MCNT@ $Ni_3(PO_4)_2$: 0.013 g MCNT, 0.018 mmol $NiSO_4 \cdot 6H_2O$, 0.032 mmol $NH_4H_2PO_4$ and 0.56 g $CO(NH_2)_2$ were slowly added in the mixture solvent of H_2O and ethylene glycol (H_2O : ethylene glycol=1:5, v/v) under mechanical magnetic stirring. Subsequently, the resultant solution was titrated to pH ~ 4.0 by hydrochloric acid and then incubated at 80 °C for 2h under continuously magnetic stirring. The obtain sample was filtered, washed with distilled water and absolute ethyl alcohol, then dried at 80 °C for 8 h, respectively.

Preparation of PS@ $Co_3(PO_4)_2$: 0.025g PS nanospheres, 0.028 mmol $CoSO_4 \cdot 7H_2O$, 0.054 mmol $NH_4H_2PO_4$ and 0.60 g $CO(NH_2)_2$ were slowly added in the mixture solvent of H_2O and ethylene glycol (H_2O : ethylene glycol=1:5, v/v) under mechanical magnetic stirring. Subsequently, the resultant solution

was titrated to pH ~ 4.0 by hydrochloric acid and then incubated at 80 °C for 2h under continuously magnetic stirring. The obtain sample was filtered, washed with distilled water and absolute ethyl alcohol, then dried at 80 °C for 8 h, respectively.

Preparation of PS@Mn₃(PO₄)₂: 0.036 g PS nanospheres, 0.025 mmol MnSO₄·H₂O, 0.046 mmol NH₄H₂PO₄ and 0.60g CO(NH₂)₂ were slowly added in the mixture solvent of H₂O and ethylene glycol (H₂O: ethylene glycol=1:5, v/v) under mechanical magnetic stirring. Subsequently, the resultant solution was titrated to pH ~ 4.0 by hydrochloric acid and then incubated at 80 °C for 2h under continuously magnetic stirring. The obtain sample was filtered, washed with distilled water and absolute ethyl alcohol, then dried at 80 °C for 8 h, respectively.

Preparation of Co-LNMO cathode material: 0.020 mmol CoSO₄·7H₂O, 0.046 mmol NH₄H₂PO₄ and 0.64 g CO(NH₂)₂ were slowly dispersed in the mixture solvent of H₂O and ethylene glycol (H₂O: ethylene glycol=1:5, v/v) under mechanical magnetic stirring. Subsequently, tuning the pH of the prepared light pink solution above to 4.0 by hydrochloric acid. Then 1.02 g of pristine LNMO powders were added into the mixture solution to obtain black turbid solution. After that, the black turbid solution was heated at 80 °C for 2 h under continuously magnetic stirring. The obtain sample was filtered, washed with distilled water and absolute ethyl alcohol, then dried at 80 °C for 8 h and annealed at 700 °C for 2 h, respectively.

Materials Characterizations

The morphology of prepared samples were characterized by using a Field Emission Scanning Electron Microscopy (FE-SEM, Hitachi S-4800) operated at 10 kV and a JEOL-2100F instrument microscopy at an acceleration voltage of 200 kV. X-ray diffraction (XRD) data collected on a Rigaku D/MAX-2500 with Cu K α radiation at 50 kV and 250 mA was used to measure the crystallographic structure of LNMO and Co-LNMO materials. Chemical state and composition analysis were performed by X-ray photoelectron spectroscopy (XPS) using an ESCALab 220i-XL electron spectrometer. The experiments of inductively coupled plasma-atomic emission spectroscopy (ICP-AES) were carried out on a Shimadzu type instrument (ICPE-9000). The electrochemical impedance spectroscopy (EIS) spectra of newly assembled button cell were collected with the help of an Autolab PGSTAT302N electrochemistry workstation.

Electrochemical Measurements

Electrochemical measurements were performed by assembling CR2032 coin cells in an argon-filled glove box. The cathodes were prepared by homogeneously mixing the active materials, acetylene black (Super-p), and poly(vinyl difluoride) (PVDF, Aldrich) at a weight ratio of 8:1:1 and pasting on a pure Al foil (99 %, Goodfellow), then cutting the coating Al foil into circular electrodes with diameter of 1.2 cm after dried under a vacuum at 80 °C for 10 h. The areal mass loading is about 1.90 mg/cm² on each cathode. During fabricating the coin cells, lithium metal was used as the counter and reference electrodes, polypropylene membrane (Celgard) was used as a separator and 1 M LiPF₆ in ethylenecarbonate (EC)/dimethyl carbonate (DMC)/diethyl carbonate (DEC) (1:1:1, in vol %) purchased from Kishida Chemical Co.,Ltd. was utilized as the electrolyte. Galvanostatic tests of the assembled cells were performed with a Land CT2001A battery test system between 3.0 and 5.0 V at room temperature or 55 °C. The electrochemical impedance spectroscopy (EIS) were collected in a frequency range from 100 kHz to 0.01 Hz with an amplitude of 10 mV. In addition, the experiment of transition metal dissolution was performed by following the literature procedure.⁴

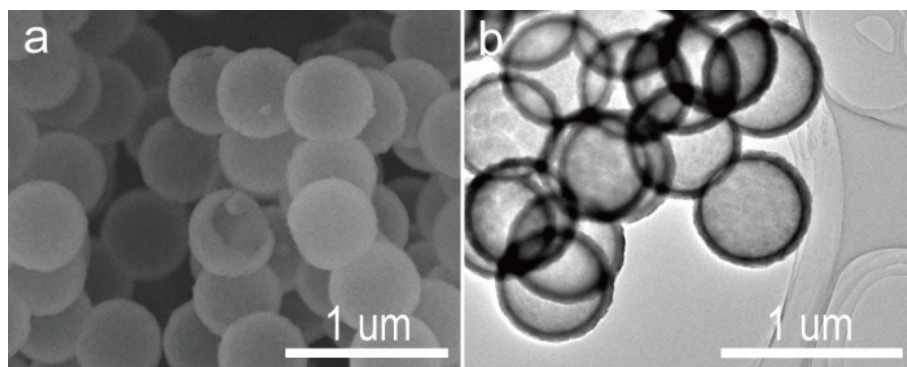


Figure S1 (a) SEM and (b)TEM images of the hollow $\text{Ni}_3(\text{PO}_4)_2$ nanospheres.

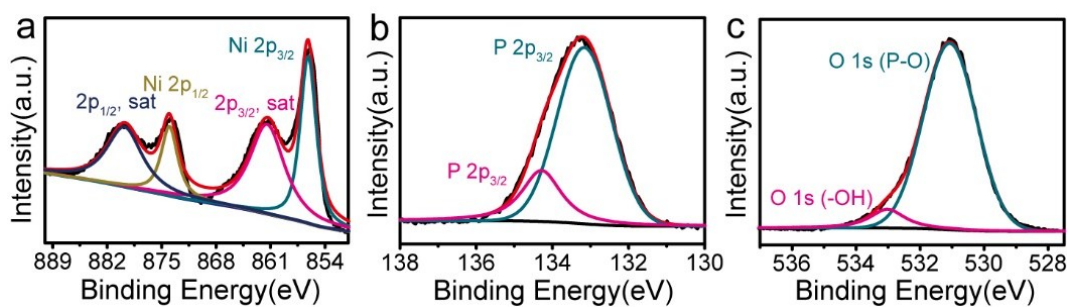


Figure S2 XPS profiles of the hollow $\text{Ni}_3(\text{PO}_4)_2$ nanospheres.

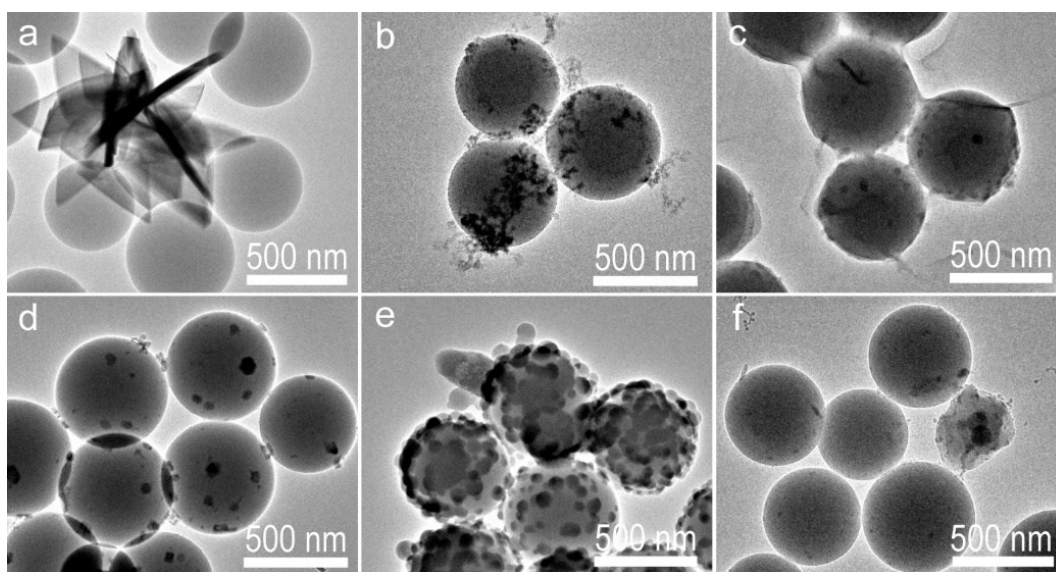


Figure S3 Different pure solvent was used to prepare $\text{PS}@ \text{Ni}_3(\text{PO}_4)_2$: (a) H_2O ; (b) Ethyl alcohol; (c) NMP; (d) DMF; (e) EG; (f) TEG.

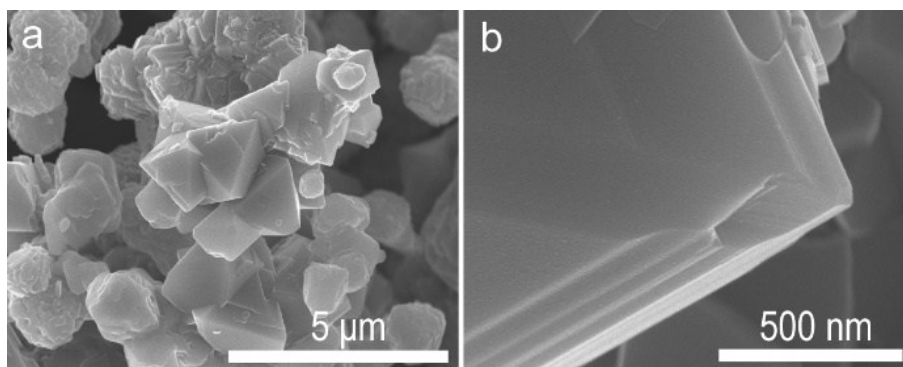


Figure S4 SEM images of the pristine LNMO.

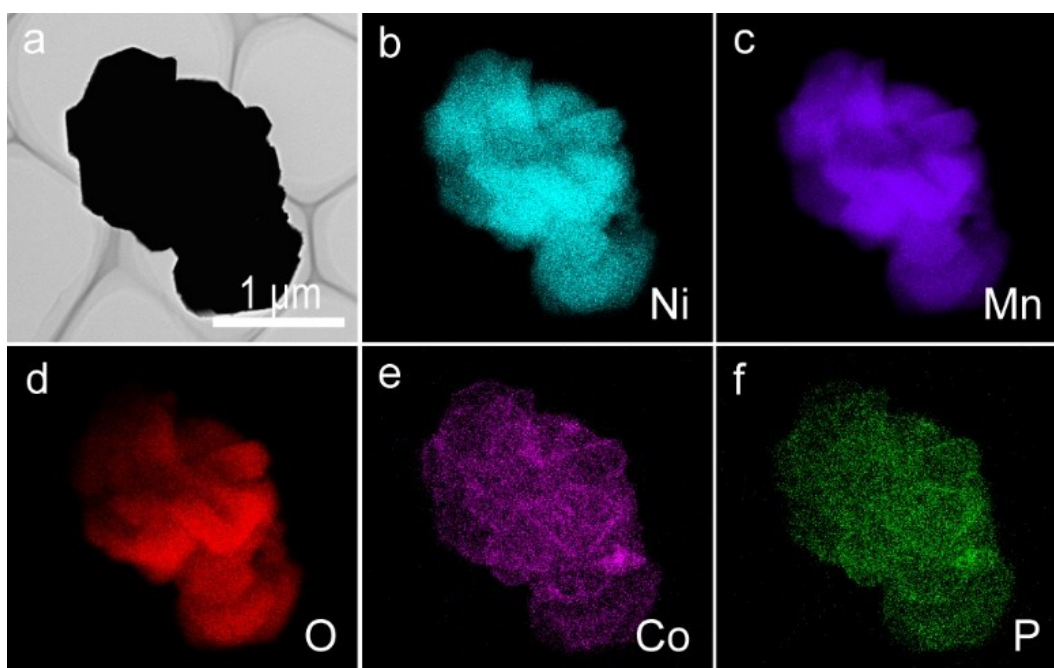


Figure S5 Elemental mappings of the LNMO@Co₃(PO₄)₂ particles for Ni, Mn, O, Co and P, respectively.

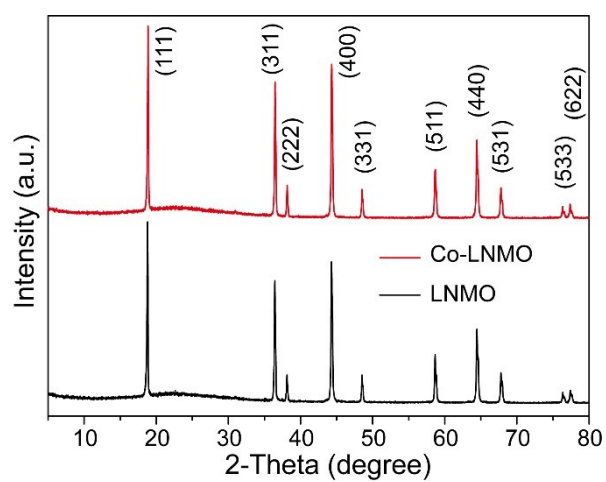


Figure S6 XRD patterns of the pristine LNMO and the Co-LNMO sample.

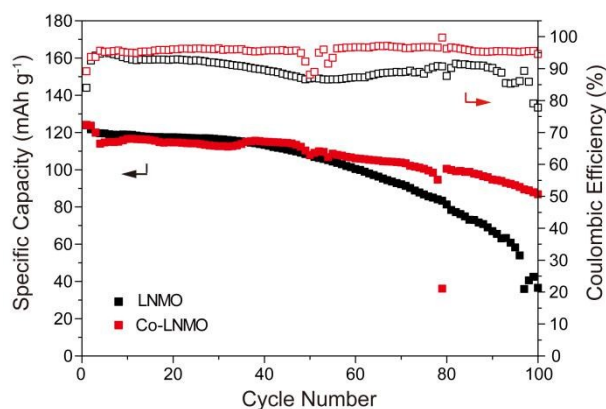


Fig. S7 Cycling performance of LNMO and Co-LNMO electrodes collected at 1.0 C at elevated temperature (60 °C).

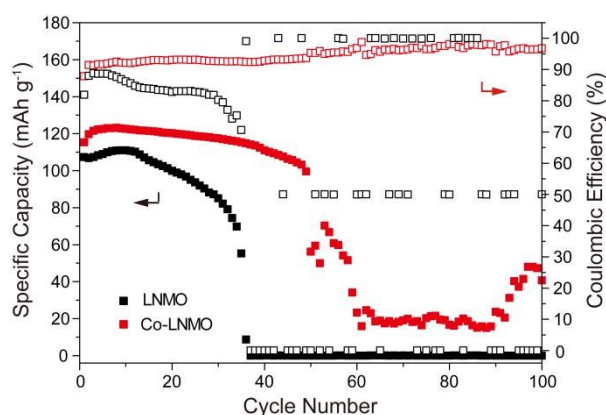


Fig. S8 Cycling performance of LNMO and Co-LNMO electrodes collected at 1.0 C at elevated temperature (70 °C).

Table S1 Elemental analysis tested by ICP-AES (based on the mass of LNMO and Co-LNMO)

Atomic ratio	Li (wt%)	Ni (wt%)	Mn (wt%)	Co (wt%)
LNMO	3.78	16.54	49.43	-
Co-LNMO	3.70	16.46	49.56	0.44

Table S2 Fitting results of the impedance spectra shown in Fig. 6e.

Impedance	R_c (Ω)	R_s (Ω)	R_{ct} (Ω)
LNMO	4.4	34.2	125.6
Co-LNMO	7.6	25.7	154.7
LNMO (after 100 cycles)	12.9	83.5	696.3
Co-LNMO (after 100 cycles)	10.6	47.4	335.2

Table S3 Mn dissolution amount tested by ICP-AES (based on the mass)

Dissolution amount	LNMO	Co-LNMO
Mn (wt%)	0.46	0.11

References

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