Supporting Information

Enabling 4.6 V LiNi_{0.6}Co_{0.2}Mn_{0.2}O₂ cathodes with excellent structural stability: combining surface LiLaO₂ self-assembly and subsurface La-pillar engineering

Zhaozhe Yu^{1,2}, Qilin Tong¹, Yan Cheng^{1,*}, Ping Yang¹, Guiquan Zhao¹, Huacheng Li¹, Weifeng An¹, Dongliang Yan¹, Xia Lu^{3,*}, Bingbing Tian^{2,*}

¹Guangxi Key Laboratory of Manufacturing Systems and Advanced Manufacturing Technology, Guilin University of Electronic Technology, Guilin 541004, Guangxi Zhuang Autonomous Region, China.

²International Collaborative Laboratory of 2D Materials for Optoelectronics Science and Technology of Ministry of Education, Institute of Microscale Optoelectronics, Shenzhen University, Shenzhen 518060, Guangdong, China.
³School of Materials, Sun Yat-Sen University, Shenzhen 518107, Guangdong, China.

*Correspondence to: Dr. Yan Cheng, Guangxi Key Laboratory of Manufacturing Systems and Advanced Manufacturing Technology, Guilin University of Electronic Technology, No. 1 Jinji Road, Qixing District, Guilin 541004, Guangxi Zhuang Autonomous Region, China. E-mail: B12030015@hnu.edu.cn; Prof. Xia Lu, School of Materials, Sun Yat-Sen University, No. 66 Gongchang Road, Xinhu Street, Guangming District, Shenzhen 518107, Guangdong, China. E-mail: luxia3@mail.sysu.edu.cn; Prof. Bingbing Tian, International Collaborative Laboratory of 2D Materials for Optoelectronics Science and Technology of Ministry of Education, Institute of Microscale Optoelectronics, Shenzhen University, No. 3688 Nanhai Avenue, Nanshan District, Shenzhen 518060, Guangdong, China. E-mail: tianbb2011@szu.edu.cn

Experimental Section

The Ni_{0.6}Co_{0.2}Mn_{0.2}(OH)₂ precursor was synthesized using a hydroxide coprecipitation method. The mixed solution (2 mol L⁻¹) containing a molar ratio of Ni:Co:Mn =6:2:2 of NiSO₄·6H₂O, CoSO₄·7H₂O and MnSO₄·5H₂O was pumped into a continuously stirred tank reactor (3 L) under inertial N₂ atmosphere. Then, 5 mol

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 L^{-1} of NaOH solution and 4 mol L^{-1} of NH₃·H₂O were added in sequence into the tank reactor. The temperature (60 °C), pH value (11.5), and stirring speed (300 rpm) of the solution were carefully controlled and maintained constant. The precursor powders were obtained through washing, filtering, and drying in a vacuum oven for 6 h to remove adsorbed water.



Supplementary Figure 1. (a) XRD enlarged images of NCM622, NCM622-La and NCM622-La@LLO (b) Local amplification of (006)/(102) and (108)/(110) peaks of XRD spectrum.



Supplementary Figure 2. The XPS comparison of La element in NCM622(a), NCM622-La(b) and NCM622-La@LLO (c).



Supplementary Figure 3. XRD refinement of NCM622(a), NCM622-La (b) and NCM622-La@LLO (c).



Supplementary Figure 4. SEM morphology images of (a) NCM622, (b) NCM622-La and (c) NCM622-La@LLO.



Supplementary Figure 5. The corresponding EDS mapping results of NCM622-La@LLO.



Supplementary Figure 6. The DOS of NCM622 (a), NCM622-La (b) and NCM622-La@LLO (c).



Supplementary Figure 7. The differential charge density of NCM622 (a) and NCM622-La (b).



Supplementary Figure 8. The differential charge density of NCM622-La@LLO



Supplementary Figure 9. GITT test diagrams of NCM622 (a), NCM622-La (b) and NCM622-La@LLO (c)



Supplementary Figure 10. CV curves of the first three cycles of (a) NCM622, (b)

NCM622-La and (c) NCM622-La@LLO



Supplementary Figure 11. Charge and discharge curves of the first three cycles of (a) NCM622, (b) NCM622-La and (c) NCM622-La@LLO

Samples	a(Å)=b (Å)	c(Å)	vol(Å ³)	Rwp (%)	Rp (%)	I(003)/I(1 04)	c/a	Ni ²⁺ in Li slab (%)
NCM622	2.8673	14. 17	100.9	11.3	8.07	1.36	4.94	4.71
NCM622-La	2.8676	17	0 100.9	12.6	8.12	1.41	4.95	2.94
		18	9					
NCM622-	2.8676	14.	100.9	14.2	8.06	1.43	4.96	2.50
La@LLO		22	9					

Supplementary Table 1. Structural parameters of the three samples from X-ray Rietveld Refinement