Supporting Information

Mitigating the P2−O2 phase transition of high-voltage P2-$Na_{2/3}[Ni_{1/3}Mn_{2/3}]O_2$ cathode by cobalt gradient substitution for high-rate sodium-ion batteries

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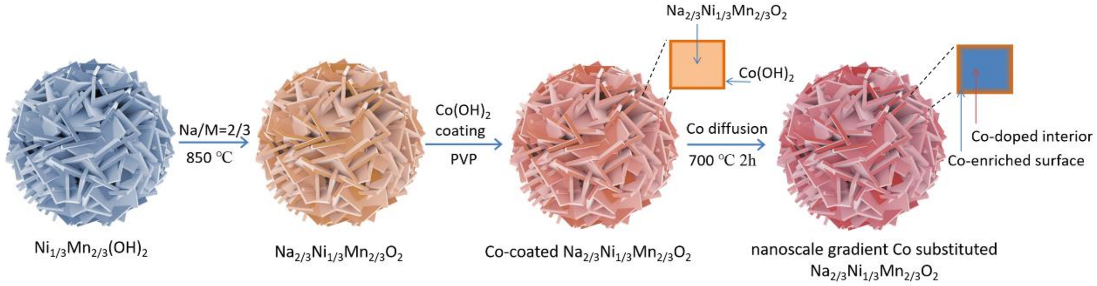

Figure S1 Schematic diagram of nanoscale gradient cobalt substituted high-voltage P2-$Na_{2/3}[Ni_{1/3}Mn_{2/3}]O_2$ *via* coating-diffusion strategy.

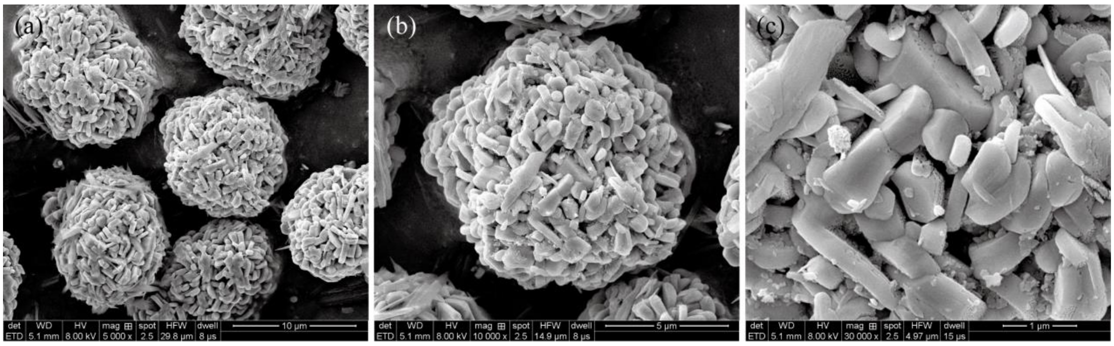

Figure S2 SEM images of the as-prepared P2-$Na_{2/3}[Ni_{1/3}Mn_{2/3}]O_2$.

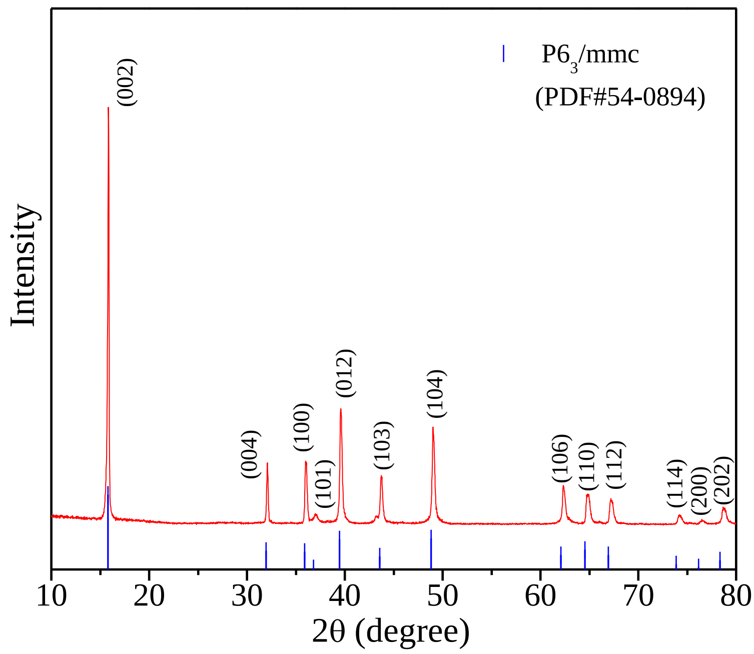

Figure S3 XRD pattern the nanoscale gradient cobalt substituted P2-$Na_{2/3}[Ni_{1/3}Mn_{2/3}]O_2$.

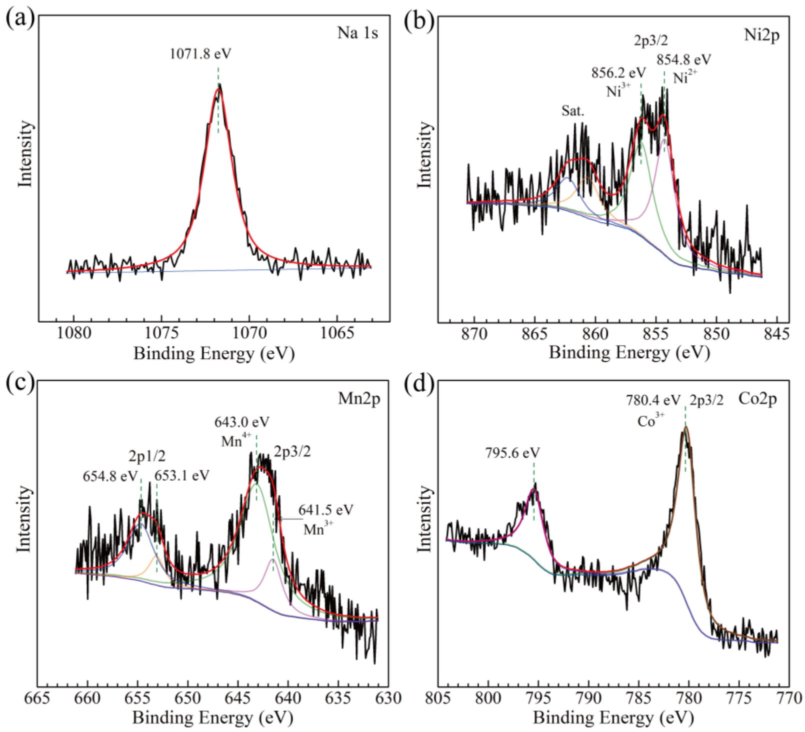

Figure S4 XPS results of the pristine nanoscale gradient Co^{3+} substituted P2-$Na_{2/3}[Ni_{1/3}Mn_{2/3}]O_2$: (a) Na 1s, (b) Ni 2p, (c) Mn 2p, and (d) Co 2p.

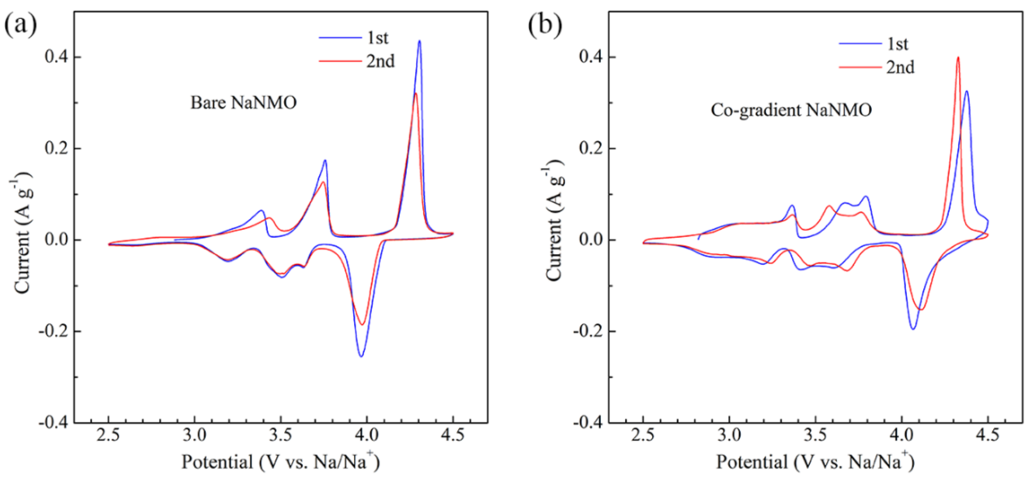

Figure S5 CV curves of the (a) bare and (b) gradient Co^{3+} substituted P2-$Na_{2/3}[Ni_{1/3}Mn_{2/3}]O_2$ between 2.5 and 4.5 V (vs. Na/Na^+) at 0.1mV s^{-1}.

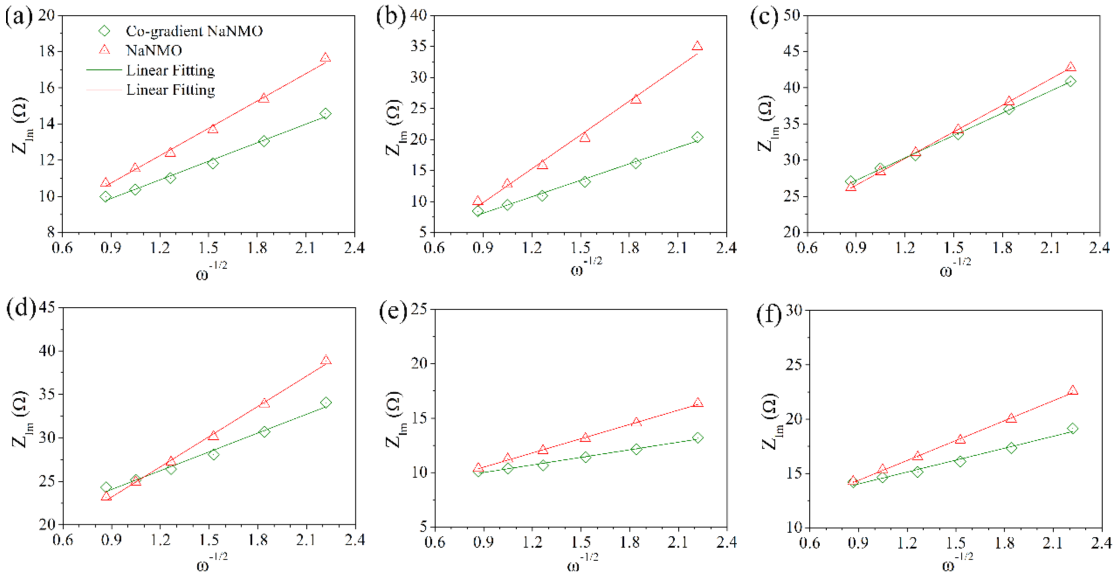

Figure S6 The relationship between Z_{im} and $\omega^{-1/2}$ in the low frequency region at varied states of charge/discharge: (a) charged to 3.5 V, (b) charged to 3.85 V, (c) charged to 4.3 V, (d) discharged to 4.1 V, (e) discharged to 3.75 V, and (f) discharged to 3.4 V.

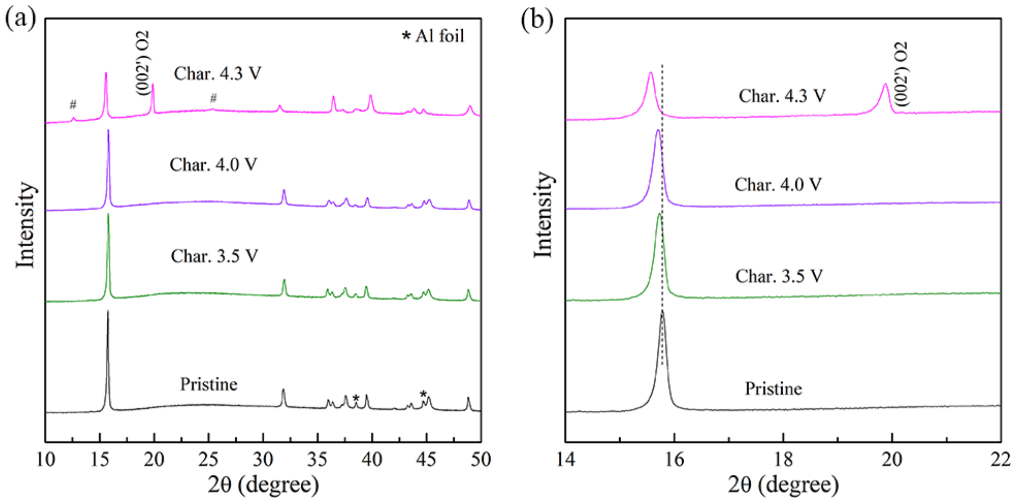

Figure S7 Ex-situ XRD analysis of the bare P2-NaNMO electrode tested at various discharge/charge states.

Table S1 Comparison of the capacity, voltage and energy density of the gradient Co^{3+} substituted P2-$Na_{2/3}[Ni_{1/3}Mn_{2/3}]O_2$ and recent reports.

Category	Structural formula	Electrochemical properties			Ref.
		Capacity (mAh g^{-1})	Voltage (V)	Energy density (Wh kg^{-1})	
P2-type	$Na_{2/3}Ni_{0.29}Co_{0.13}Mn_{0.58}O_2$	164.2	3.55	583	Our work
	$Na_{2/3}Fe_{1/2}Mn_{1/2}O_2$	190	2.75	523	S1
	$Na_{0.6}Cr_{0.6}Ti_{0.4}O_2$	75	3.45	259	S2
	$Na_{0.67}Mn_{0.67}Ni_{0.28}Mg_{0.05}O_2$	123	3.7	455	S3
	$Na_{2/3}Cu_{1/12}Ni_{1/4}Mn_{2/3}O_2$	130	3.62	471	S4
	$Na_{2/3}Ni_{0.283}Mg_{0.05}Mn_{2/3}O_2$	150	3.5	525	S5
	$Na_{2/3}Ni_{1/3}Mn_{1/3}Ti_{1/3}O_2$	90	3.5	322	S6
	$Na_{2/3}Fe_{0.2}Mn_{0.8}$O2	190	2.5	475	S7
O3-type	$NaNi_{0.45}Cu_{0.05}Mn_{0.4}Ti_{0.1}O_2$	122	3.0	366	S8
	$NaNi_{0.5}Mn_{0.2}Ti_{0.3}O_2$	140	3.0	420	S9
	$Na_{0.8}Ni_{0.4}Ti_{0.6}O_2$	85	2.8	238	S10
	$NaNi_{0.6}Co_{0.05}Mn_{0.35}O_2$	145	2.5	363	S11
	$NaLi_{0.05}Mn_{0.50}Ni_{0.30}Cu_{0.10}Mg_{0.05}O_2$	172	2.75	473	S12
	$NaCrO_2$	120	3.0	360	S13
	$Na_3Ni_{1.5}Cu_{0.5}BiO_6$	92	3.2	294	S14
Polyanion	$Na_3V_2(PO_4)_3$	115	3.4	391	S15
	$Na_3V_2(PO_4)_2F_3$	116	3.6	418	S16
	$Na_3V_2(PO_4)_2O_2F$	127.8	3.8	486	S17
	$NaVOPO_4$	144	3.5	504	S18
	$NaFePO_4$	146	2.4	350	S19
Prussian blues	$Na_{1.89}Mn[Fe(CN)_6]_{0.97}$	150	3.5	525	S20
	$Na_{0.61}FeFe(CN)_6$	170	3.0	510	S21
Organics	$Na_4C_8H_2O_6$	180	1.8	324	S22
	$Na_2C_6O_6$	192	2.1	403	S23

The Na^+ diffusion coefficient (D_{Na+}) can be calculated according to the following Equation:

$D_{Na+} = (R^2T^2)/(2A^2n^4F^4C^2\delta^2)$

where R is the gas constant (8.314 J K^{-1} mol^{-1}), T is the absolute temperature (298.15 K), A is the surface area of the electrode (0.785 cm^2), n is the number of the electrons per molecule during oxidization (here, n=1), F is the Faraday constant (96500 C mol^{-1}), C is the concentration of Na^+ ($4.12\times10^{-2}\times(0.76\text{-}x)$ mol cm^{-3}, x indicates the extracted Na^+ in $Na_{2/3}[Ni_{1/3}Mn_{2/3}]O_2$) and δ is the Warburg factor (Ω $s^{-1/2}$) associated with Z_{im} (the imaginary part of cell impedance, ohm) and ω (the frequency, Hz), calculated by Equation:

$Z_{im} \propto \delta\omega^{-1/2}$

Table S2 The calculated Na^+ diffusion coefficient (D_{Na+}) during charge processes.

Samples	Na^+ diffusion coefficient (D_{Na+})			
	Charged 3.45 V (cm^2 s^{-1})	Charged 3.85 V (cm^2 s^{-1})	Charged 4.3 V (cm^2 s^{-1})	Average (cm^2 s^{-1})
Bare NaNMO	1.88×10^{-12}	4.14×10^{-13}	2.37×10^{-11}	8.66×10^{-12}
Co-gradient NaNMO	4.06×10^{-12}	1.76×10^{-12}	3.59×10^{-11}	1.34×10^{-11}

Table S3 The calculated Na^+ diffusion coefficient (D_{Na+}) during discharge processes.

Samples	Na^+ diffusion coefficient (D_{Na+})			
	Discharged 4.1 V (cm^2 s^{-1})	Discharged 3.75 V (cm^2 s^{-1})	Discharged 3.4 V (cm^2 s^{-1})	Average (cm^2 s^{-1})
Bare NaNMO	1.89×10^{-12}	7.52×10^{-12}	1.71×10^{-12}	3.71×10^{-12}
Co-gradient NaNMO	4.92×10^{-12}	2.66×10^{-11}	4.76×10^{-12}	1.21×10^{-11}

References

S1 N. Yabuuchi, M. Kajiyama, J. Iwatate, H. Nishikawa, S. Hitomi, R. Okuyama, R. Usui, Y. Yamada and S. Komaba, *Nat. Mater.*, 2012, 11, 512−518.

S2 Y. Wang, R. Xiao, Y. Hu, M. Avdeev and L. Chen, *Nat. Comm.*, 2015, 6, 6954.

S3 P. Wang, Y. You, Y. Yin, Y. Wang, L. Wan, L. Gu and Y. Guo, *Angew. Chem. Int. Ed.*, 2016, 55, 7445 –7449.

S4 L. Zheng, J. Li and M. N. Obrovac, *Chem. Mater.*, 2017, 29(4), 1623–1631.

S5 N. Tapia-Ruiz, W. M. Dose, N. Sharma, H. Chen, J. Heath, J. Somerville, U. Maitra, M. S. Islam and P. G. Bruce, *Energy Environ. Sci.*, 2018,11, 1470-1479.

S6 P. Wang, H. Yao, X. Liu, Y. Yin, J. Zhang, Y. Wen, X. Yu, L. Gu, Y. Guo, *Sci. Adv.*, 2018; 4: eaar6018.

S7 W. M. Dose, N. Sharma, J. C. Pramudita, H. E. A. Brand, E. Gonzalo and T. Rojo, *Chem. Mater.*, 2017, 29, 7416−7423.

S8 H.-R. Yao, P.-F. Wang, Y. Gon, J. Zhang, X. Yu, L. Gu, C. OuYang, Y.-X. Yin, E. Hu, X.-Q. Yang, E. Stavitski, Y.-G. Guo and L.-J. Wan, *J. Am. Chem. Soc.*, 2017, 139, 8440–8443.

S9 P. Wang, H. Yao, X. Liu, J. Zhang, L. Gu, X. Yu, Y. Yin and Y. Guo, *Adv. Mater.*, 2017, 29, 1700210.

S10 S. Guo, H. Yu, P. Liu, Y. Ren, T. Zhang, M. Chen, M. Ishida, H. Zhou, *Energy Environ. Sci.*, 2015,8, 1237-1244.

S11 J. Hwang, S. Oh, S. Myung, K. Y. Chung, I. Belharouak and Y. Sun, *Nat. Comm.*, 2015, 6, 6865.

S12 J. Deng, W. Luo, X. Lu, Q. Yao, Z. Wang, H. Liu, H. Zhou and S. Dou, *Adv. Energy Mater.*, 2018, 8, 1701610.

S13 C. Yu, J. Park, H. Jung, K. Chung, D. Aurbachd, Y. Sun and S. Myung, *Energy Environ. Sci.*, 2015,8, 2019-2026.

S14 P. Wang, Y. Guo, H. Duan, T. Zuo, E. Hu, K. Attenkofer, H. Li, X. S. Zhao, Y. Yin, X. Yu, and Y. Guo, *ACS Energy Lett.*, 2017, 2, 2715–2722.

S15 Y. Fang, L. Xiao, X. Ai, Y. Cao and H. Yang, *Adv. Mater.*, 2015, 27, 5895-5900

S16 C. Zhu, C. Wu, C. Chen, P. Kopold, P. A. van Aken, J. Maier and Y. Yu, *Chem. Mater.*, 2017, 29, 5207–5215.

S17 J. Guo, P. Wang, X. Wu, X. Zhang, Q. Yan, H. Chen, J. Zhang and Y. Guo, *Adv. Mater.*, 2017, 29, 1701968.

S18 Y. Fang, Q. Liu, L. Xiao,Y. Rong, Y. Liu, Z. Chen, X. Ai, Y. Cao, H. Yang, J. Xie, C. Sun, X. Zhang, B. Aoun, X. Xing, X. Xiao and Y. Ren, *Chem*, 2018, 4, 1167-1180.

S19 M. Rahman, I. Sultana, S. Mateti, J. Liu, N. Sharmab and Y. Chen, *J. Mater. Chem. A*, 2017, 5,16616.

S20 J. Song, L. Wang, Y. Lu, J. Liu, B. Guo, P. Xiao, J. Lee, X. Yang, G. Henkelman and J. B. Goodenough, *J. Am. Chem. Soc*., 2015, 137, 2658–2664.

S21 J. Qian, C. Wu, Y. Cao, Z. Ma, Y. Huang, X. Ai and H. Yang, *Adv. Energy Mater.*, 2018, 8, 1702619.

S22 Wang, L. Wang, Z. Zhu, Z. Hu, Q. Zhao and J. Chen, *Angew. Chem. Int. Ed*., 2014, 53, 5892-5896.

S23 Y. Wang, Y. Ding, L. Pan, Y. Shi, Z. Yue, Y. Shi and G. Yu, *Nano Lett.*, 2016, 16, 3329–3334