Electronic Supplementary Information (ESI)

Novel P2-type $Na_{2/3}Ni_{1/6}Mg_{1/6}Ti_{2/3}O_2$ as an anode material for sodium-ion batteries

Peng-Fei Wang,[ab] Hu-Rong Yao,[ab] Tong-Tong Zuo,[ab] Ya-Xia Yin,[↑ab] and Yu-Guo Guo[↑ab]

[a] CAS Key Laboratory of Molecular Nanostructure and Nanotechnology, and Beijing National Laboratory for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences (CAS), Beijing 100190, P.R. China.

[b] School of Chemistry and Chemical Engineering, University of Chinese Academy of Sciences, Beijing 100049, P.R. China.

↑ To whom correspondence should be addressed. E-mail: ygguo@iccas.ac.cn; yxyin@iccas.ac.cn.

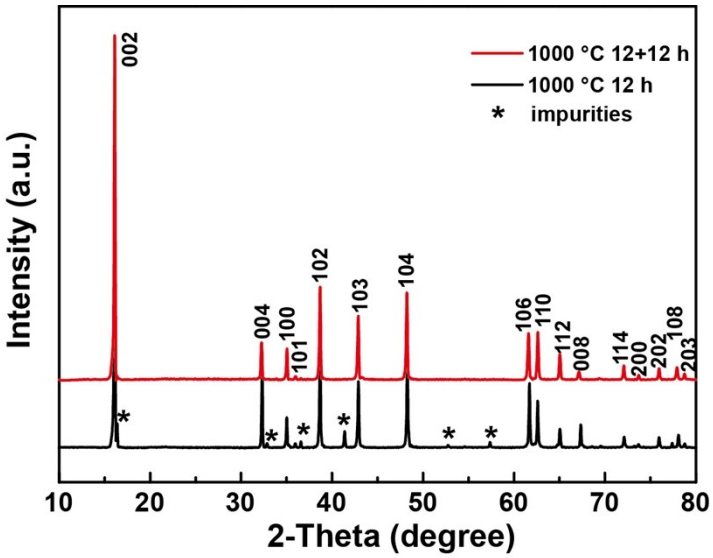

Fig. S1 Powder X-ray diffraction pattern of P2-type $Na_{2/3}Ni_{1/6}Mg_{1/6}Ti_{2/3}O_2$ samples.

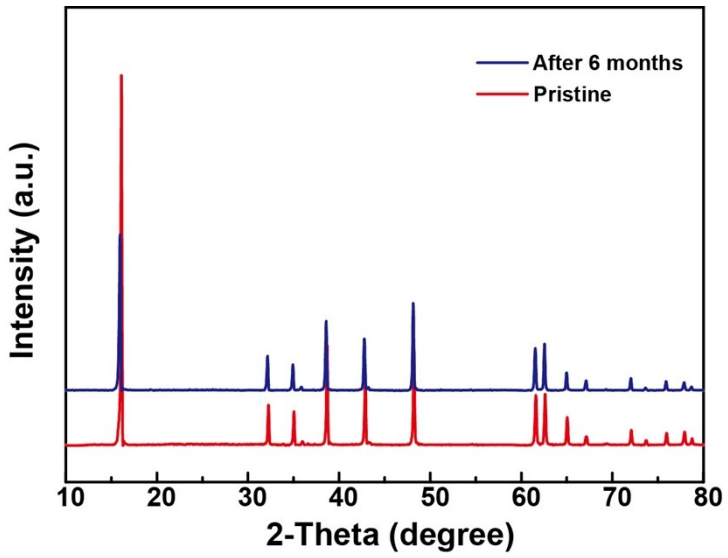

Fig. S2 Powder X-ray diffraction pattern demonstrating structural stability of P2-type $Na_{2/3}Ni_{1/6}Mg_{1/6}Ti_{2/3}O_2$ after different days on exposure to air.

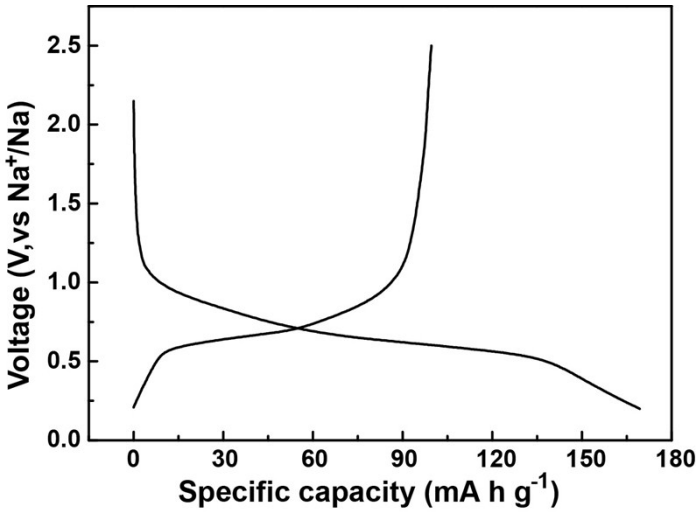

Fig. S3 The first discharge/charge curves of P2-$Na_{2/3}Ni_{1/6}Mg_{1/6}Ti_{2/3}O_2$ electrodes cycled at a current rate of 0.1 C in the voltage range of 0.2-2.5 V.

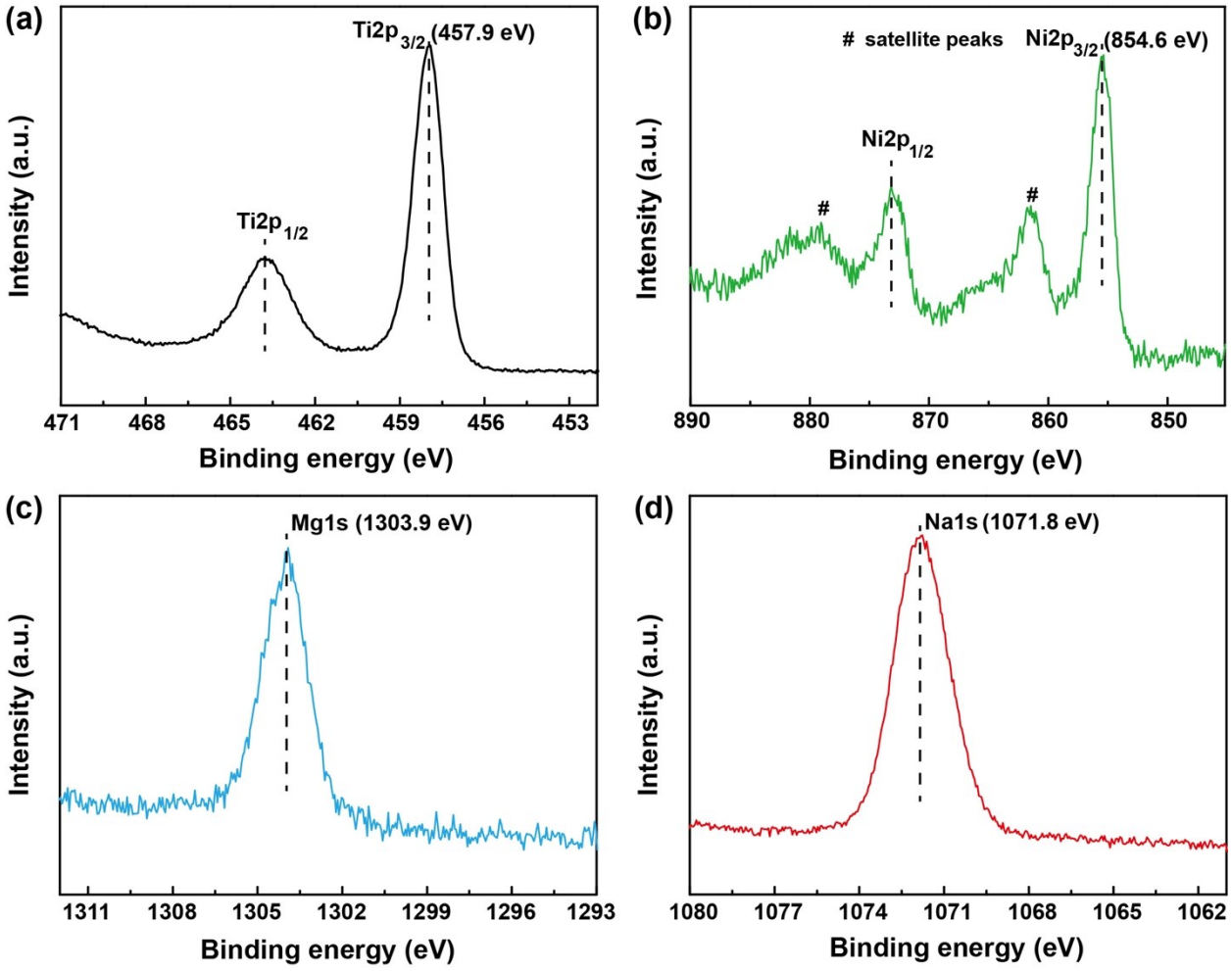

Fig. S4 XPS spectra of P2-$Na_{2/3}Ni_{1/6}Mg_{1/6}Ti_{2/3}O_2$ for (a) Ti2p, (b) Ni2p, (c)Mg1s and (d) Na1s regions, indicating titanium, nickel, magnesium and sodium elements are in a valence state of +4, +2, +2 and +1, respectively.

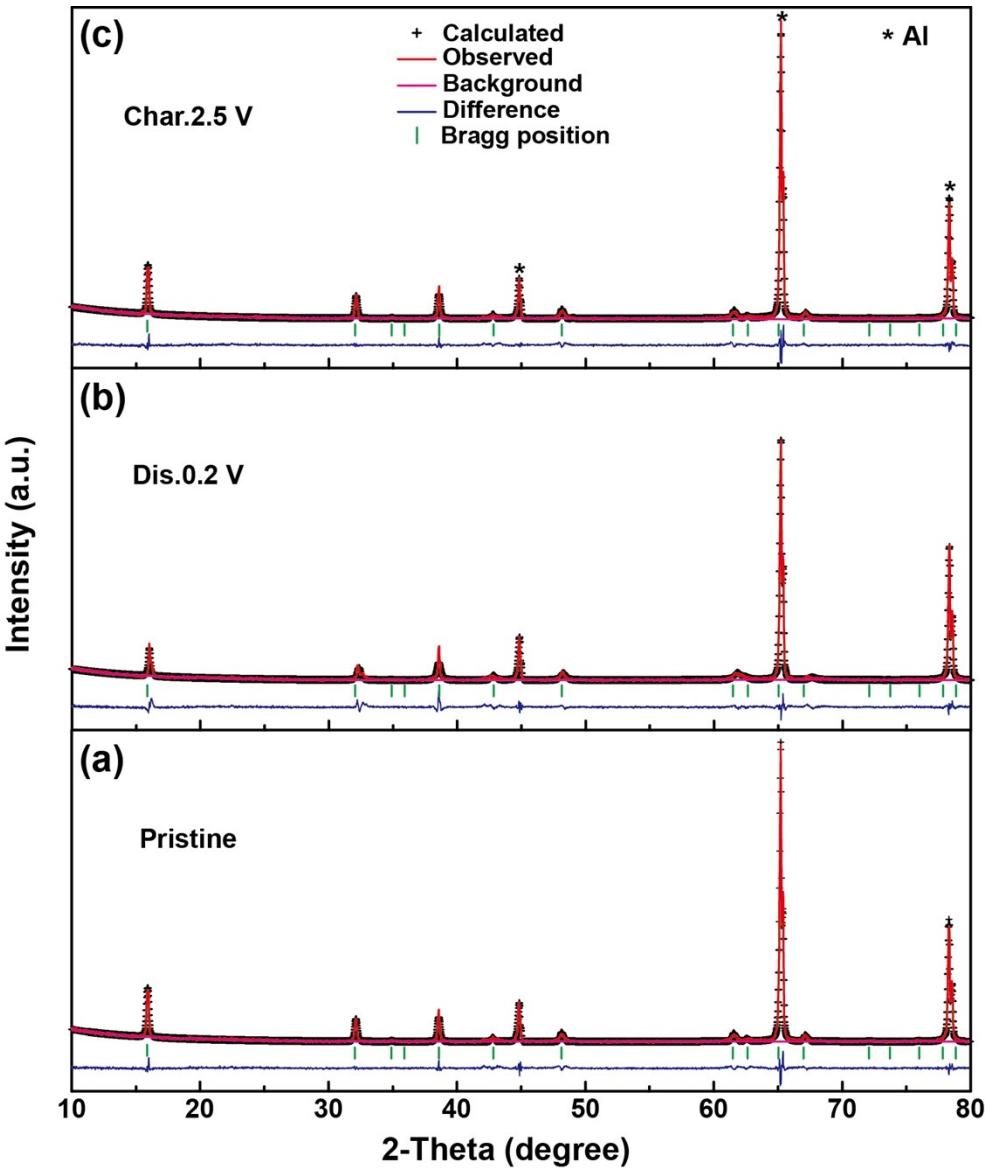

Fig. S5 *In situ* XRD patterns and Rietveld refinement P2-$Na_{2/3}Ni_{1/6}Mg_{1/6}Ti_{2/3}O_2$ electrodes at different discharge/charge states during the first cycle.

Table S1. Crystallographic parameters of P2-$Na_{2/3}Ni_{1/6}Mg_{1/6}Ti_{2/3}O_2$ refined by the Rietveld method.

Atom	**Site**	**x**	**y**	**z**	**Occ.**
Na_e	2d	1/3	2/3	1/4	0.443
Na_f	2b	0	0	1/4	0.227
Ni	2a	0	0	0	0.167
Mg	2a	0	0	0	0.166
Ti	2a	0	0	0	0.667
O	4f	2/3	1/3	0.0931	1.000
$P6_3/mmc$	a = 2.9680(2) Å	c = 11.146(5) Å	V=85.036(6) $Å^3$	R_p=5.7 %	R_{wp}=7.5 %

Table S2: Comparison of electrode performance of titanium-based P2-type anodes for sodium-ion batteries.

Materials	Different element	Practical capacity (mA h g^{-1})	Cycling stability	Average voltage (V)	Reference
P2-$Na_{2/3}Ni_{1/3}Ti_{2/3}O_2$	Ni	75 (0.05 C, 0.2-2.0 V)	67% (25 cycles)	0.7	29
P2-$Na_{0.66}[Li_{0.22}Ti_{0.78}]O_2$	Li (expensive)	100 (0.1 C, 0.4-2.5 V)	75% (1200 cycles)	0.75	30
P2-$Na_{2/3}Co_{1/3}Ti_{2/3}O_2$	Co (expensive)	90 (0.2 C, 0.15-2.5 V)	84.84% (3000 cycles)	0.7	31
P2-$Na_{0.6}[Cr_{0.6}Ti_{0.4}]O_2$	Cr (poisonous)	105 (0.1 C, 0.5-2.5 V)	90.4% (200 cycles)	0.8	32
P2-$Na_{2/3}Ni_{1/6}Mg_{1/6}Ti_{2/3}O_2$	Mg (cheap)	92 (0.1 C, 0.2-2.5 V)	87.4% (100 cycles)	0.7	This work

Table S3: Crystal parameters refined by the Rietveld method on the *in situ* XRD patterns of pristine P2-$Na_{2/3}Ni_{1/6}Mg_{1/6}Ti_{2/3}O_2$ and electrochemically cycled samples.

	Pristine	**Discharged. 0.2 V**	**Charged. 2.5 V**
Composition	$Na_{2/3}Ni_{1/6}Mg_{1/6}Ti_{2/3}O_2$	$NaNi_{1/6}Mg_{1/6}Ti_{2/3}O_2$	$Na_{2/3}Ni_{1/6}Mg_{1/6}Ti_{2/3}O_2$
Space group	$P6_3/mmc$	$P6_3/mmc$	$P6_3/mmc$
Cell parameters			
a [Å]	2.9680(2)	2.9751(9)	2.9691(9)
c [Å]	11.146(5)	11.134(3)	11.149(8)
V [$Å^3$]	85.036(6)	85.353(4)	85.128(0)
Agreement factors			
R_{wp}	7.5%	8.9%	7.6%
R_p	5.7%	5.3%	5.4%