Supplementary Material

P2-layered $Na_{0.5}Li_{0.07}Mn_{0.61}Co_{0.16}Ni_{0.16}O_2$ cathode boosted Na-storage properties by rational sub-group element doping

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Table S1 Elemental composition from ICP-OES results.

Theoretical chemical formula	Measured atomic ratio							
	Na	Li	Mn	Co	Ni	Cu	Ag	Au
$Na_{0.5}Li_{0.07}Mn_{0.61}Co_{0.16}Ni_{0.16}O_2$	0.506	0.069	0.614	0.165	0.160	0.000	0.000	0.000
$Na_{0.5}Li_{0.07}Mn_{0.6}Co_{0.16}Ni_{0.16}Cu_{0.01}O_2$	0.507	0.072	0.604	0.157	0.162	0.013	0.000	0.000
$Na_{0.5}Li_{0.07}Mn_{0.6}Co_{0.16}Ni_{0.16}Ag_{0.01}O_2$	0.501	0.068	0.607	0.161	0.157	0.000	0.014	0.000
$Na_{0.5}Li_{0.07}Mn_{0.6}Co_{0.16}Ni_{0.16}Au_{0.01}O_2$	0.503	0.071	0.598	0.167	0.161	0.000	0.000	0.011

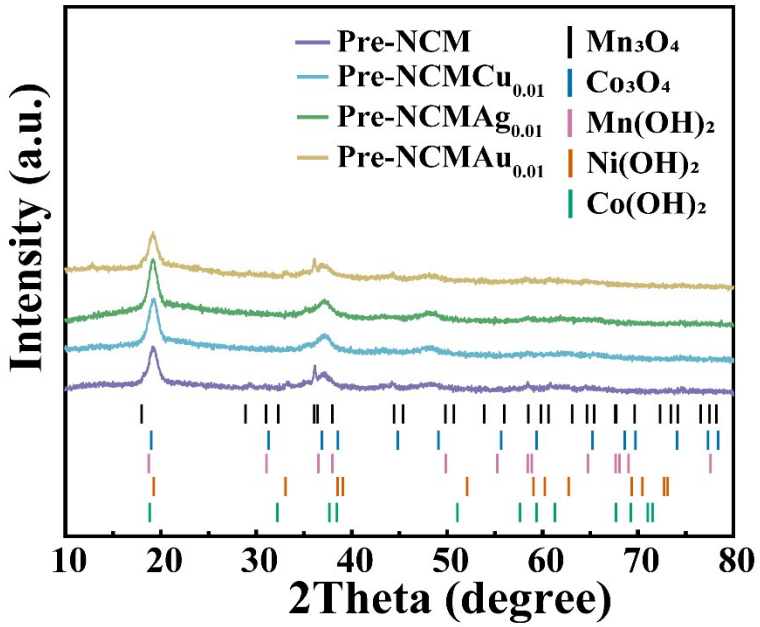

Fig. S1 Powder X-ray diffraction pattern of the precursors.

Table S2 Refined results of NCM, $NCMCu_{0.01}$, $NCMAg_{0.01}$, and $NCMAu_{0.01}$ samples.

Samples	a/b(Å)	c(Å)	V(Å^3)	Na-O(Å)	TM-O(Å)	R_{wp}(%)	R_p(%)	chi^2
NCM	2.85469(6)	11.19946(19)	79.0397(28)	2.550(3)	1.8564(16)	3.50	2.40	1.297
$NCMCu_{0.01}$	2.85515(6)	11.20068(18)	79.0737(27)	2.575(3)	1.8417(16)	3.52	2.46	1.382
$NCMAg_{0.01}$	2.85561(8)	11.20130(20)	79.0958(28)	2.591(3)	1.8320(17)	4.35	3.03	1.378
$NCMAu_{0.01}$	2.85602(6)	11.20399(20)	79.1453(28)	2.609(3)	1.8234(16)	4.06	2.87	1.299

Table S3 Crystallographic parameters of four samples refined by the Rietveld refinement.

Materials	Atom	Site	X	Y	Z	Occ
NCM	Mn	2a	0	0	0	0.61
	Co	2a	0	0	0	0.16
	Ni	2a	0	0	0	0.16
	Na_e	2d	1/3	2/3	3/4	0.25
	Na_f	2b	0	0	1/4	0.25
	Li	2a	0	0	0	0.07
	O	4f	1/3	2/3	0.07628(32)	1
$NCMCu_{0.01}$	Mn	2a	0	0	0	0.60
	Co	2a	0	0	0	0.16
	Ni	2a	0	0	0	0.16
	Cu	2a	0	0	0	0.01
	Na_e	2d	1/3	2/3	3/4	0.25
	Na_f	2b	0	0	1/4	0.25
	Li	2a	0	0	0	0.07
	O	4f	1/3	2/3	0.07334(31)	1
$NCMAg_{0.01}$	Mn	2a	0	0	0	0.60
	Co	2a	0	0	0	0.16
	Ni	2a	0	0	0	0.16
	Ag	2a	0	0	0	0.01
	Na_e	2d	1/3	2/3	3/4	0.25
	Na_f	2b	0	0	1/4	0.25
	Li	2a	0	0	0	0.07
	O	4f	1/3	2/3	0.06949(33)	1
$NCMAu_{0.01}$	Mn	2a	0	0	0	0.60
	Co	2a	0	0	0	0.16
	Ni	2a	0	0	0	0.16
	Au	2a	0	0	0	0.01
	Na_e	2d	1/3	2/3	3/4	0.25
	Na_f	2b	0	0	1/4	0.25
	Li	2a	0	0	0	0.07
	O	4f	1/3	2/3	0.06949(33)	1

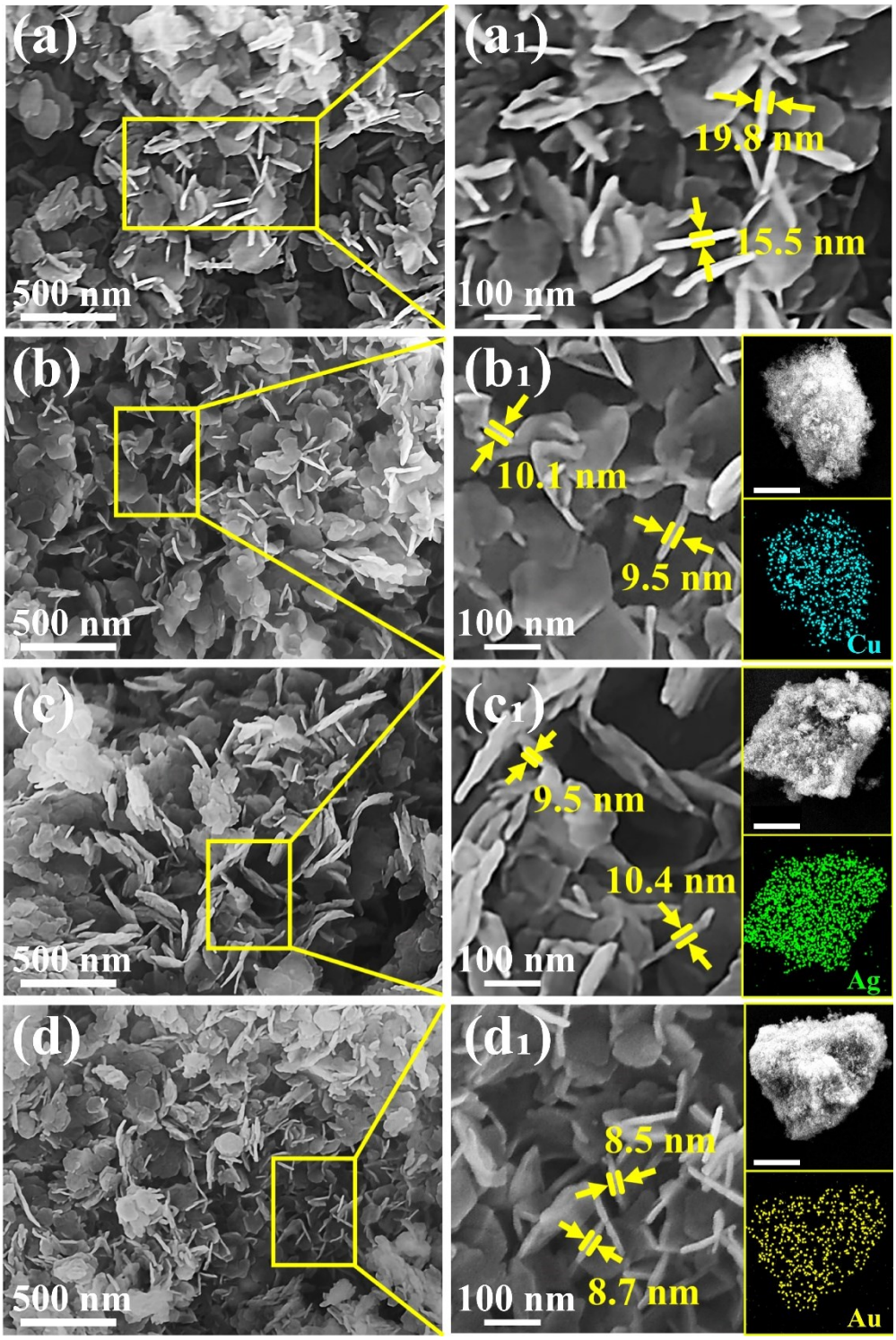

Fig. S2 SEM images with different magnifications and corresponding EDS mapping of as-prepared (a, a_1) Pre-NCM, (b, b_1) Pre-NCM$Cu_{0.01}$, (c, c_1) Pre-NCM$Ag_{0.01}$ and (d, d_1) Pre-NCM$Au_{0.01}$ precursors. (The scales of all insets are 10 μm)

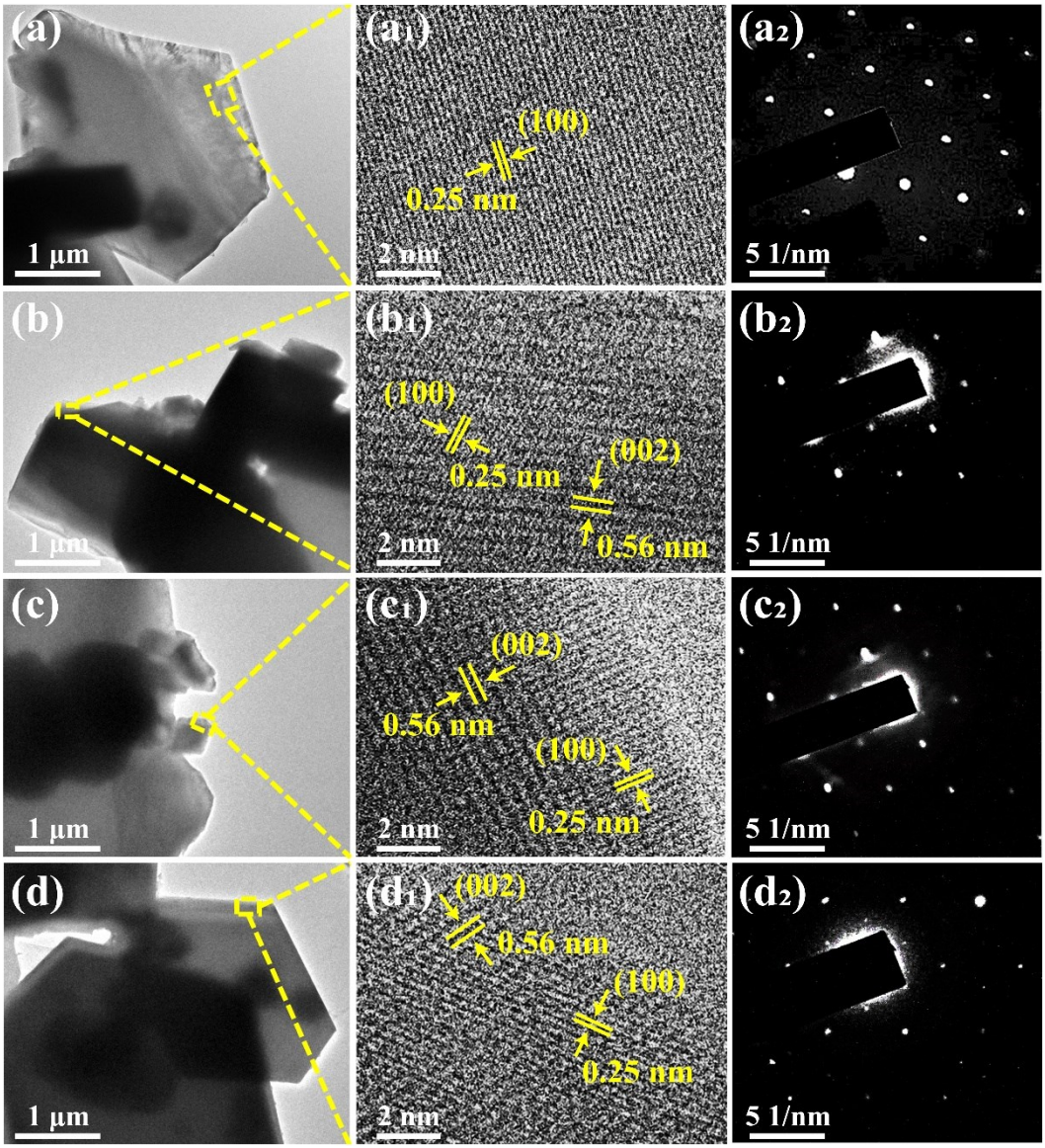

Fig. S3 TEM, high-resolution TEM images and corresponding SAED patterns of as-prepared (a, a_1, a_2) NCM, (b, b_1, b_2) $NCMCu_{0.01}$, (c, c_1, c_2) $NCMAg_{0.01}$ and (d, d_1, d_2) $NCMAu_{0.01}$ samples.

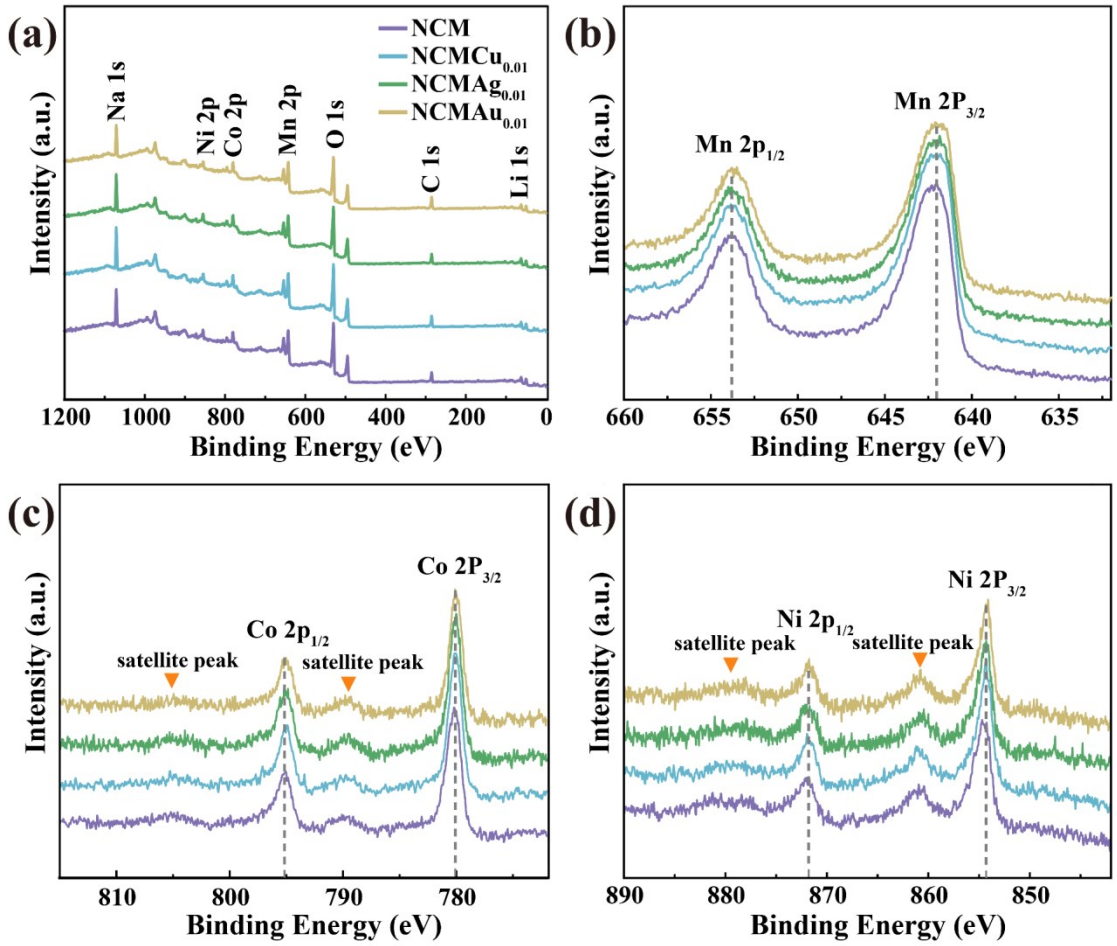

Fig. S4 XPS spectra of NCM, $NCMCu_{0.01}$, $NCMAg_{0.01}$ and $NCMAu_{0.01}$ samples: (a) The survey spectrum, (b)Mn 2p, (c)Co 2p, and (d)Ni 2p.

Table S4 The fitting results of four samples from EIS curves.

Sample	R_s/Ω	R_f/Ω	R_{ct}/Ω	i_0/(mA cm^{-2})
NCM	2.40	8.77	427.8	5.31×10^{-2}
$NCMCu_{0.01}$	2.00	5.78	618.7	3.67×10^{-2}
$NCMAg_{0.01}$	1.95	5.47	315.9	7.19×10^{-2}
$NCMAu_{0.01}$	1.91	4.43	264.0	8.61×10^{-2}

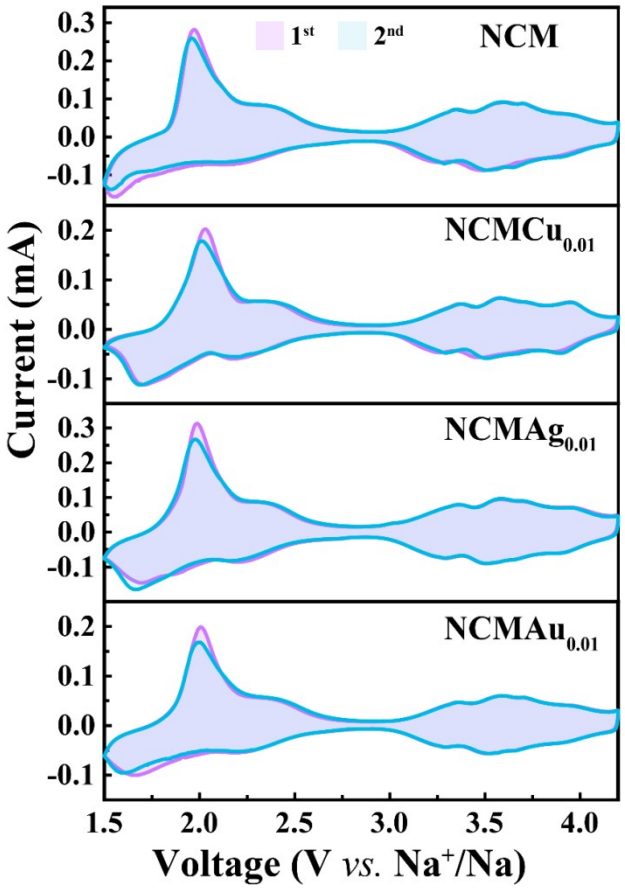

Fig. S5 The CV curves at a scan rate of 0.1 mV s^{-1} in the voltage range of 1.5- 4.2 V.

Table S5 Comparison results of three different space-occupying for Au^{+} via Rietveld refinement.

Samples	a/b(Å)	c(Å)	V(Å3)	R_{wp}(%)	R_p(%)	chi^2
NCM	2.85469(6)	11.19946(19)	79.0397(28)	3.50	2.40	1.297
$NCMAu_{0.01}$-2b	2.85303(17)	11.17476(28)	78.774(7)	6.35	3.94	2.740
$NCMAu_{0.01}$-2d	——	——	——	——	——	——
$NCMAu_{0.01}$-2a	2.85602(6)	11.20399(20)	79.1453(28)	4.06	2.87	1.299

Table S6 Comparison results of three different space-occupying for Au^{+} via Rietveld refinement.

Materials	Atom	Site	X	Y	Z	Occ
	Mn	2a	0	0	0	0.60
	Co	2a	0	0	0	0.16
	Ni	2a	0	0	0	0.16
$NCMAu_{0.01}$-2b	Au	2b	0	0	1/4	0.01
	Na_e	2d	1/3	2/3	3/4	0.25
	Na_f	2b	0	0	1/4	0.24
	Li	2a	0	0	0	0.07
	O	4f	1/3	2/3	0.0683(4)	1
	Mn	2a	0	0	0	0.60
	Co	2a	0	0	0	0.16
	Ni	2a	0	0	0	0.16
$NCMAu_{0.01}$-2d	Au	2d	1/3	2/3	3/4	0.01
	Na_e	2d	1/3	2/3	3/4	0.24
	Na_f	2b	0	0	1/4	0.25
	Li	2a	0	0	0	0.07

	O	4f	1/3	2/3	0.0872	1
	Mn	2a	0	0	0	0.60
	Co	2a	0	0	0	0.16
	Ni	2a	0	0	0	0.16
$NCMAu_{0.01}$-2a	Au	2a	0	0	0	0.01
	Na_e	2d	1/3	2/3	3/4	0.25
	Na_f	2b	0	0	1/4	0.25
	Li	2a	0	0	0	0.07
	O	4f	1/3	2/3	0.06949(33)	1

Table S5 and S6 compare the refinement results of Au^+ doping into different locations. Firstly, we hypothesis the Au^+ doped to the site of Na^+, there are two situations as below: (1) When Au^+ occupying the Na_f position (labeled as $NCMAu_{0.01}$-2b), the refinement results of the lattice parameters a/b, c and V are not only smaller than undoped NCM, but also the convergence of the refinement results is inferior to undoped NCM. Additionally, this assumption is not consistent with the facts because the radius of Au^+ is larger than the Na^+; (2) When the Na_e position is occupied by Au^+ ($NCMAu_{0.01}$-2d), the refinement results are divergent; (3) When the Au^+ occupies the transition metal position ($NCMAu_{0.01}$-2a), the unit cell parameters and unit cell volume are larger than undoped NCM, the refinement result is convergent, these results are consistent with the fact of large Au^+ radius. In view of the above-mentioned facts and discussion, Au^+ and Ag^+ should occupy the sites of transition metals.