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Supporting Information

Effects of ammonia on microstructure and crystallinity of Nickel-based carbonate materials

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Fig. S1. Schematic of set-up for the synthesis of Ni-based carbonate materials.

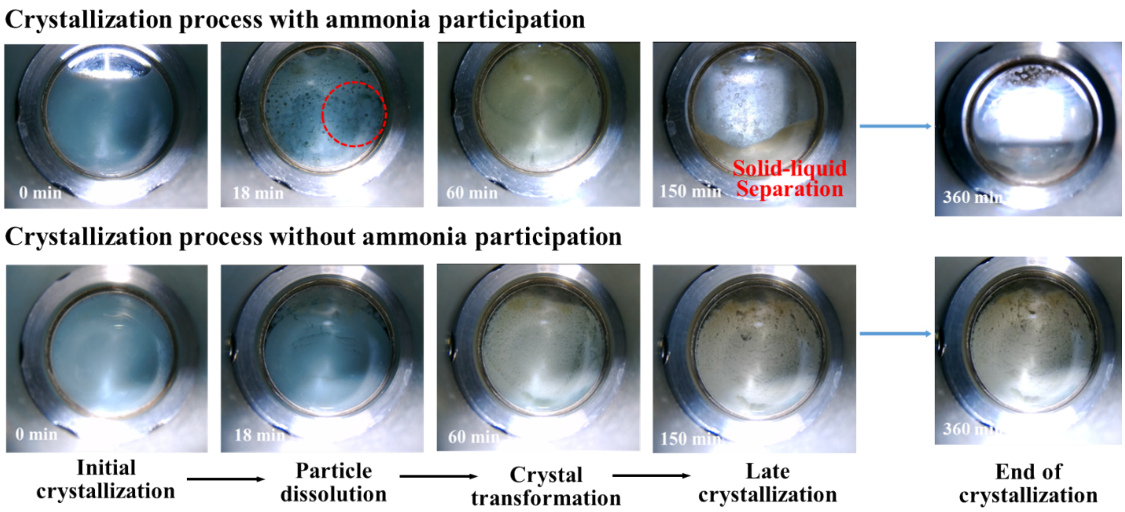

Fig. S2. Visual images of MCO_3 after hydrothermal crystallizations with different times, with or without ammonia participation.

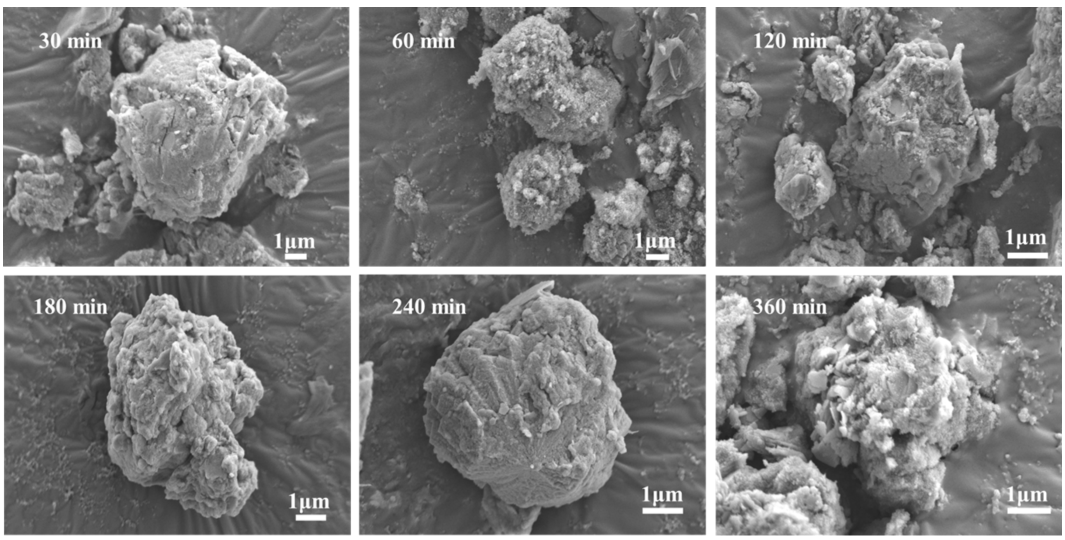

Fig. S3. The SEM images of MCO_3 after hydrothermal crystallizations with different times without ammonia participation.

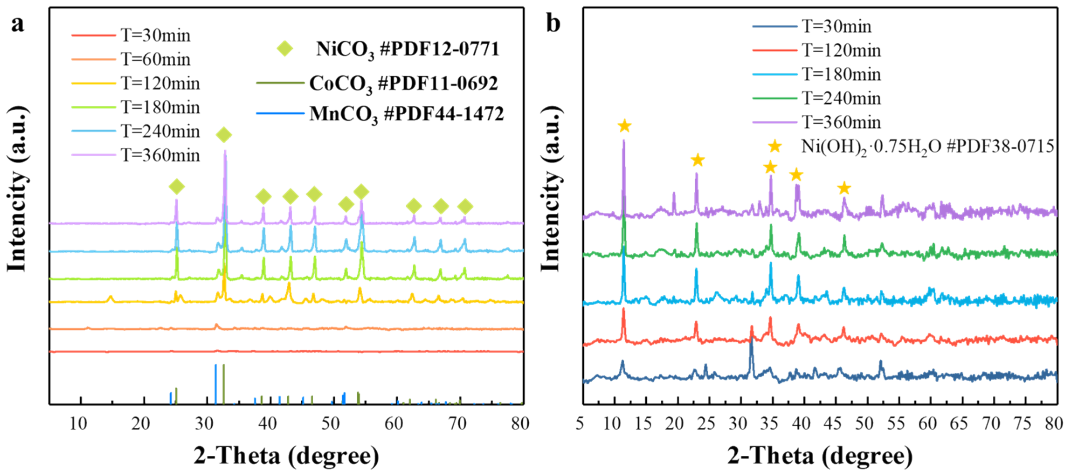

Fig. S4. The XRD spectra of MCO_3 after hydrothermal crystallizations with different times: (a) with ammonia; (b) without ammonia participation.

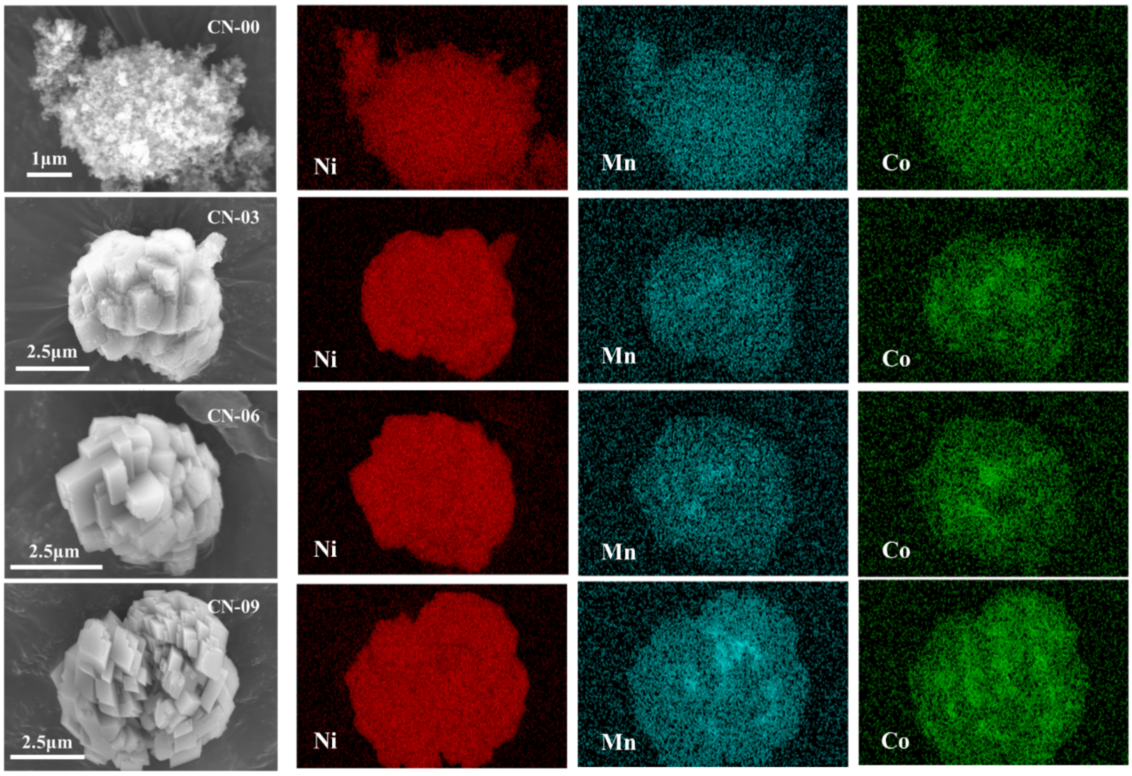

Fig. S5. The SEM image and corresponding EDS mappings of the CN-X samples.

Measurements method of ammonia Concentrations in solution

Indophenol blue absorptiometry has been utilized for measuring ammonia concentrations. A mixture of 1 mL of filtered solution, 1 mL of 0.5M H_2SO_4 solution, 5 mL of sodium phenate, and 1 mL of sodium hypochlorite was prepared in a 10 mL volumetric flask and subsequently diluted with distilled water. This solution was then placed in a quartz cell, and its absorbance spectrum at 630 nm was measured using an absorptiometer. The ammonia concentrations were determined by referencing a calibration curve.[1]

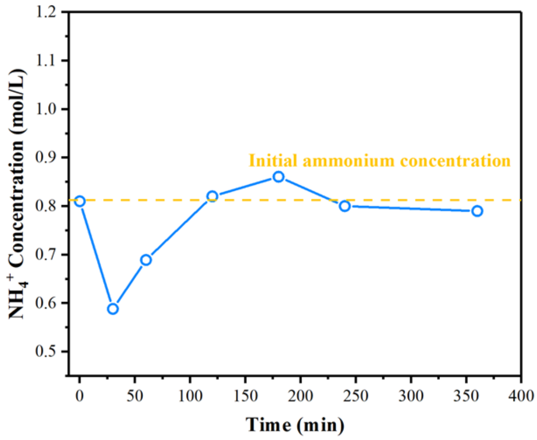

Fig. S6. The curves of ammonia concentration for MCO_3 at different reaction times (C_{NH3}=0.9 M, T=180 °C).

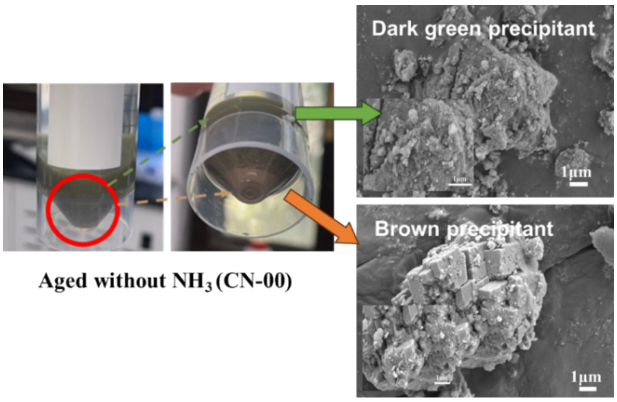

Fig. S7 The SEM images of precipitants with different appearances (sample CN-00).

Theoretical calculation method

Precipitation reaction and complexation reaction mainly occur in the M^{2+}-NH_3-CO_3^{2-}-H_2O system. The reaction equations related to the transition metal precipitation are listed as Eqs. (S1)-(S4):

$$M^{2+} + CO_3{}^{2-} = MCO_3(s) \quad K_{sp} = [M^{2+}][CO_3{}^{2-}] \tag{Eq. S1}$$

$$[C] = [CO_3{}^{2-}] + [HCO_3{}^{-}] + [H_2CO_3] \tag{Eq. S2}$$

$$[CO_3{}^{2-}] = [C]/(1 + 10^{-10.35 - pH} + 10^{16.68 - 2pH}) \tag{Eq. S3}$$

$$[M^{2+}] = K_{sp}/[CO_3{}^{2-}] \tag{Eq. S4}$$

where K_{sp} represents the equilibrium constant of carbonate, [C] represents the total carbon content in solution.

Since the carbonate solution is usually a weakly alkaline solution, there will be a hydroxide precipitation reaction process in the solution, and the formation equations are listed in Eqs. S5-S6.

$$M^{2+} + 2OH^- = M(OH)_2(s) \quad K_{sp} = [M^{2+}][OH^-]^2 \qquad \text{Eq. S5}$$

$$[M^{2+}] = K_{sp}/(10^{28+2pH}) \qquad \text{Eq. S6}$$

The carbonate precipitation reaction and hydroxide precipitation reaction in the solution are competitive reactions, so the concentration of free metal ions in the solution is

$$[M^{2+}] = \min\{K_{sp}/[{CO_3}^{2-}], K_{sp}/(K_w^2 10^{2pH})\} \qquad \text{Eq. S7}$$

The transition metal ions undergo a complexation reaction with the ligand as shown in Eq. S8.

$$M + L = ML \qquad [ML] = \beta_1[M][L]$$

$$M + 2L = ML_2 \qquad [ML_2] = \beta_2[M][L]^2$$

…… ……

$$M + nL = ML_n \qquad [ML_n] = \beta_2[M][L]^n \qquad \text{Eq. S8}$$

Where M represents the transitional ions, β_n the complexation reaction constant, n the number of ligands.

The calculation formula of Gibbs free energy ΔG is shown in Eq. 9:

$$\Delta G_{Mc} = RTlnK_{spMc} - RT\ln([M^{2+}][{CO_3}^{2-}]) \qquad \text{Eq. S9}$$

Table. S1 Equilibrium reactions and constants in Ni^{2+}-NH_3-CO_3^{2-}-H_2O[2]

No.	Equation	lg*K*	No.	Equation	lg*K*
1	$H_2CO_3 = H^+ + HCO_3^-$	-6.35	21	$Co^{2+} + 3OH^- = Co(OH)_3^-$	10.5
2	$HCO_3^- = H^+ + CO_3^{2-}$	-10.33	22	$Co^{2+} + 4OH^- = Co(OH)_3^-$	10.2
3	$NH_3 + H^+ = NH_4^+$	9.25	23	$2Co^{2+} + OH^- = Co_2(OH)^{3+}$	2.7
4	$H_2O = H^+ + OH^-$	-14.0	24	$Co^{2+} + NH_3 = Co(NH_3)^{2+}$	2.11
5	$NiCO_3(s) = Ni^{2+} + CO_3^{2-}$	-6.85	25	$Co^{2+} + 2NH_3 = Co(NH_3)_2^{2+}$	3.74
6	$Ni(OH)_2(s) = Ni^{2+} + 2OH^-$	-15.26	26	$Co^{2+} + 3NH_3 = Co(NH_3)_3^{2+}$	4.79
7	$Ni^{2+} + OH^- = Ni(OH)^+$	4.97	27	$Co^{2+} + 4NH_3 = Co(NH_3)_4^{2+}$	5.55
8	$Ni^{2+} + 2OH^- = Ni(OH)_2^0$	8.55	28	$Co^{2+} + 5NH_3 = Co(NH_3)_5^{2+}$	5.73
9	$Ni^{2+} + 3OH^- = Ni(OH)_3^-$	11.33	29	$Co^{2+} + 6NH_3 = Co(NH_3)_6^{2+}$	5.11
10	$2Ni^{2+} + OH^- = Ni_2(OH)^{3+}$	3.3	30	$MnCO_3(s) = Mn^{2+} + CO_3^{2-}$	-10.63
11	$Ni^{2+} + NH_3 = Ni(NH_3)^{2+}$	2.8	31	$Mn(OH)_2(s) = Mn^{2+} + 2OH^-$	-12.72
12	$Ni^{2+} + 2NH_3 = Ni(NH_3)_2^{2+}$	5.04	32	$Mn^{2+} + OH^- = Mn(OH)^+$	3.9
13	$Ni^{2+} + 3NH_3 = Ni(NH_3)_3^{2+}$	6.7	33	$Mn^{2+} + 3OH^- = Mn(OH)_3^-$	8.3
14	$Ni^{2+} + 4NH_3 = Ni(NH_3)_4^{2+}$	7.96	34	$Mn^{2+} + 4OH^- = Mn(OH)_3^-$	7.7
15	$Ni^{2+} + 5NH_3 = Ni(NH_3)_5^{2+}$	8.71	35	$2Mn^{2+} + OH^- = Mn_2(OH)^{3+}$	3.4

16	$Ni^{2+} + 6NH_3 = Ni(NH_3)_6^{2+}$	8.74	36	$Mn^{2+} + NH_3 = Mn(NH_3)^{2+}$	0.8
17	$CoCO_3(s) = Co^{2+} + CO_3^{2-}$	-12.84	37	$Mn^{2+} + 2NH_3 = Mn(NH_3)_2^{2+}$	1.3
18	$Co(OH)_2(s) = Co^{2+} + 2OH^-$	-14.23	38	$Mn^{2+} + 3NH_3 = Mn(NH_3)_3^{2+}$	1.7
19	$Co^{2+} + OH^- = Co(OH)^+$	3.3	39	$Mn^{2+} + 4NH_3 = Mn(NH_3)_4^{2+}$	1.3
20	$Co^{2+} + 2OH^- = Co(OH)_2^0$	9.2			

The total concentrations of metal ions $[M^{2+}]_T$ are calculated by the sum of the concentrations of free metal ions. Meanwhile, total concentrations of ammonia $[NH_3]_T$ can be obtained according to the following equations.

$$[M^{2+}]_T = [M^{2+}] + \sum_{n=1}^{6}\left[M(NH_3)_n^{\ 2+}\right] + \sum_{n=1}^{6}\left[M(NH_3)_n^{\ 2+}\right] + \sum_{n=1}^{4}[M(OH)_n^{\ 2-n}] \quad \text{Eq. S10}$$

$$[NH_3]_T = [NH_3] + [NH_4^{\ +}] + \sum\left[M(NH_3)_n^{\ 2+}\right] \quad \text{Eq. S11}$$

$$[Ni^{2+}] = [Ni^{2+}]\{1 + 10^{2.8}[NH_3] + 10^{5.04}[NH_3]^2 + 10^{6.77}[NH_3]^3 + 10^{7.96}[NH_3]^4 + 10^{8.71}[NH_3]^5 + 10^{8.74}[NH_3]^6 + 10^{pH - 9.03} + 10^{2pH - 19.45} + 10^{3pH - 30.67} \quad \text{Eq. S12}$$

$$[Co^{2+}]_T = [Co^{2+}]\{1 + 10^{2.11}[NH_3] + 10^{3.74}[NH_3]^2 + 10^{4.79}[NH_3]^3 + 10^{5.55}[NH_3]^4 + 10^{5.73}[NH_3]^5 + 10^{5.11}[NH_3]^6 + 10^{pH - 10.7} + 10^{2pH - 18.8} + 10^{3pH - 31.5} + 10^{4pH - 53.8} \quad \text{Eq. S13}$$

$$[Mn^{2+}]_T = [Mn^{2+}]\{1 + 10^{0.8}[NH_3] + 10^{1.3}[NH_3]^2 + 10^{1.7}[NH_3]^3 + 10^{1.3}[NH_3]^4 + 10^{pH - 10.01} + 10^{3pH - 33.7} + 10^{4pH - 56.3} \quad \text{Eq. S14}$$

$$[NH_3]_T = [NH_3]\{1 + 10^{9.27 - pH} + 10^{10.78 - pH}\left[CO_3^{\ 2-}\right] + 10^{2.8}[Ni^{2+}] + 10^{5.04}[Ni^{2+}][NH_3] + 10^{6.77}[Ni^{2+}][NH_3]^2 + 10^{7.96}[Ni^{2+}][NH_3]^3 + 10^{8.71}[Ni^{2+}][NH_3]^4 + 10^{8.74}[Ni^{2+}][NH_3]^5 + 10^{2.11}[Co^{2+}] + 10^{3.74}[Co^{2+}][NH_3] + 10^{4.79}[Co^{2+}][NH_3]^2 + 10^{5.55}[Co^{2+}][NH_3]^3 + 10^{5.73}[Co^{2+}][NH_3]^4 + 10^{5.11}[Co^{2+}][NH_3]^5 + 10^{0.8}[Mn^{2+}] + 10^{1.3}[Mn^{2+}][NH_3] + 10^{1.7}[Mn^{2+}][NH_3]^2 + 10^{1.3}[Co^{2+}][NH_3]^3 \quad \text{Eq. S15}$$

Suppose [C] and $[NH_3]_T$ are certain values in the solution, according to the thermodynamic models with considerations on the reactions above, the values of $[M^{2+}]_T$ *vs* pH can be calculated through Eqs. S7, S12-15.

Then, the concentration of metal-ammonia complex $[Ni(NH_3)_n^{2+}]$ can be calculated with following formula[3].

$$\left[Ni(NH_3)_n^{\ 2+}\right] = [Ni^{2+}]_T - [Ni^{2+} \quad \text{Eq. S16}$$

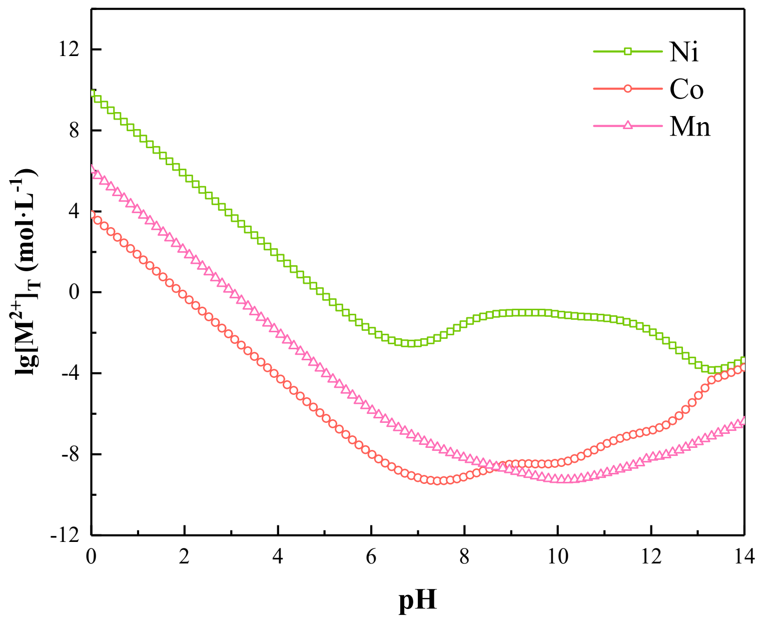

Fig. S8. Plots of lg[M^{2+}]$_T$ (M=Ni, Co, Mn) *vs* pH.

Reference

1. K. Funakoshi, S. Yoshizawa and M. Matsuoka, *Crystal Growth & Design*, 2016, **16**, 1824-1828.
2. A. D. John, *Lange's handbook of chemistry, Fifthenth Edition, Mc. Graw Hill Inc, New York. Conference*, 1999.
3. Y. Shen, Y. Wu, H. Xue, S. Wang, D. Yin, L. Wang and Y. Cheng, *ACS Applied Materials & Interfaces*, 2021, **13**, 717-726.