Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Electronic Supporting Information

Facile and template-free fabrication of mesoporous 3D nanospheres-like $Mn_xCo_{3-x}O_4$ as highly effective catalysts for low temperature SCR of NO_x with NH_3

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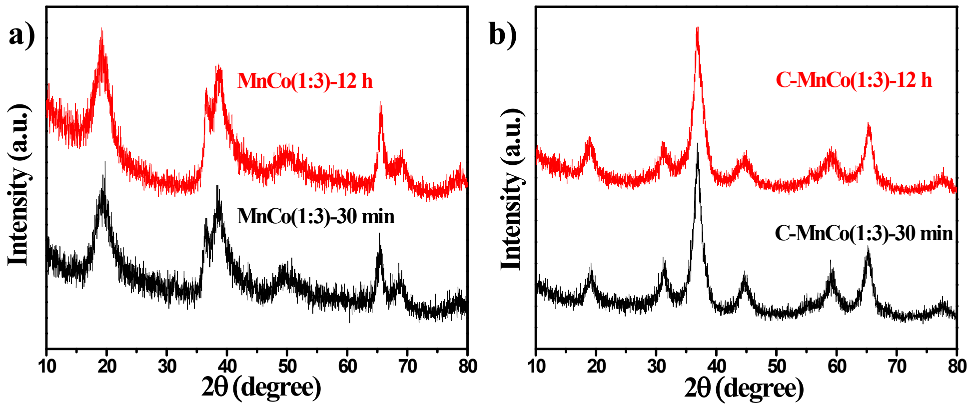


Fig. S1. XRD patterns of MnCo(1:3) prepared for 30 min and 12 h before (a) and after (b) calcination.

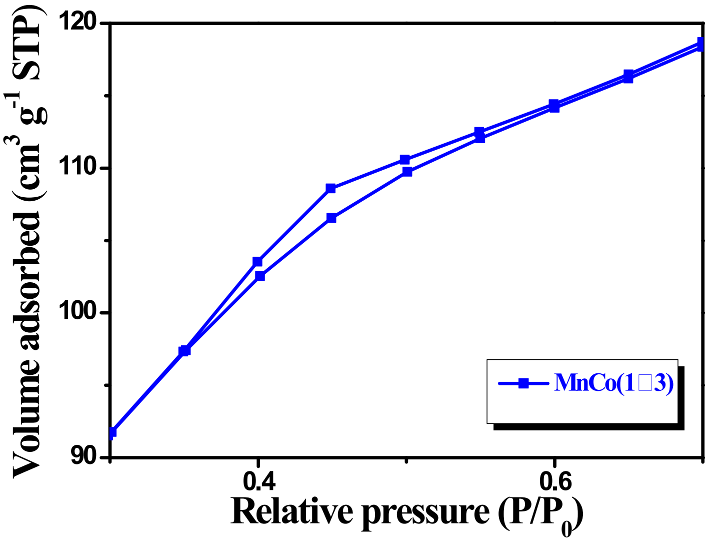


Fig. S2. The enlarged N_2 adsorption-desorption isotherms of MnCo(1:3).

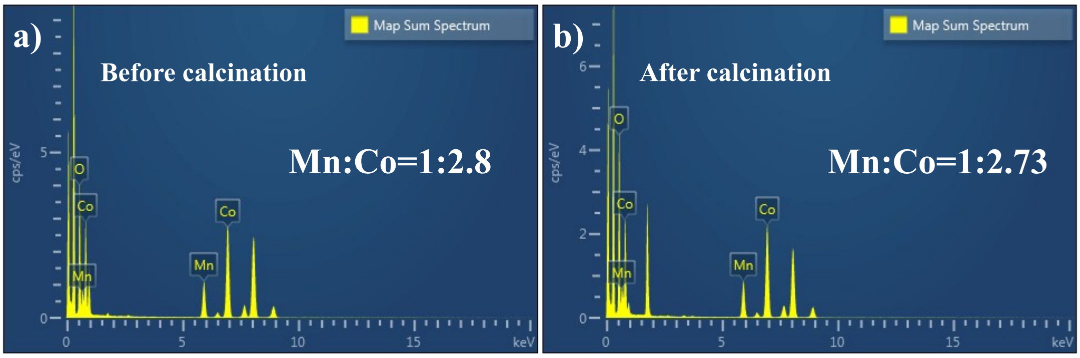


Fig. S3. EDX spectrum of MnCo(1:3) (a) and C-MnCo(1:3) (b).

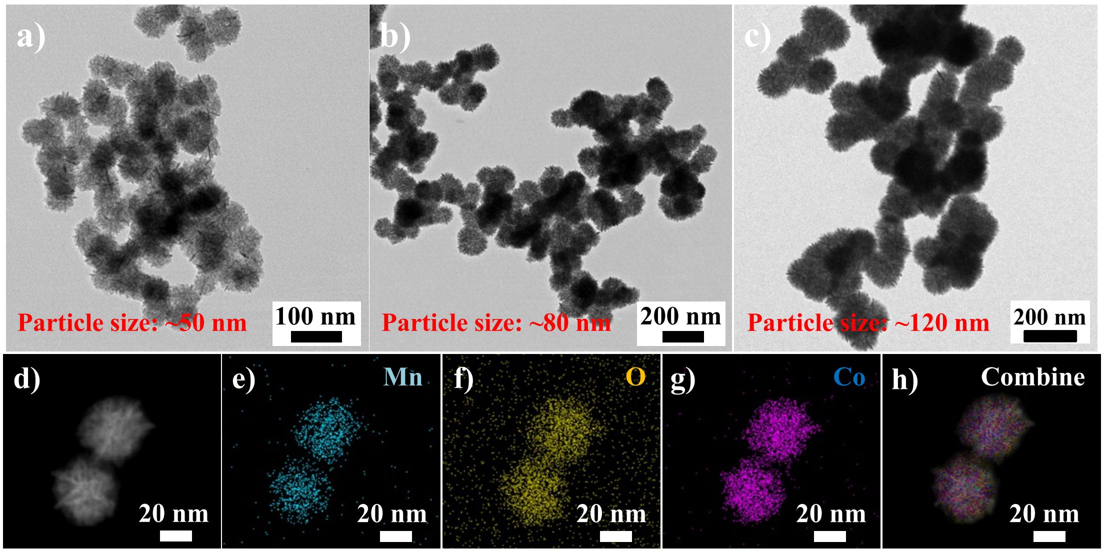


Fig. S4. TEM images of C-MnCo(1:3) collected at different durations: a) 1 min, b) 20 min and c) 30 min. The corresponding EDX-mapping of C-MnCo(1:3) prepared for 1min (d-h).

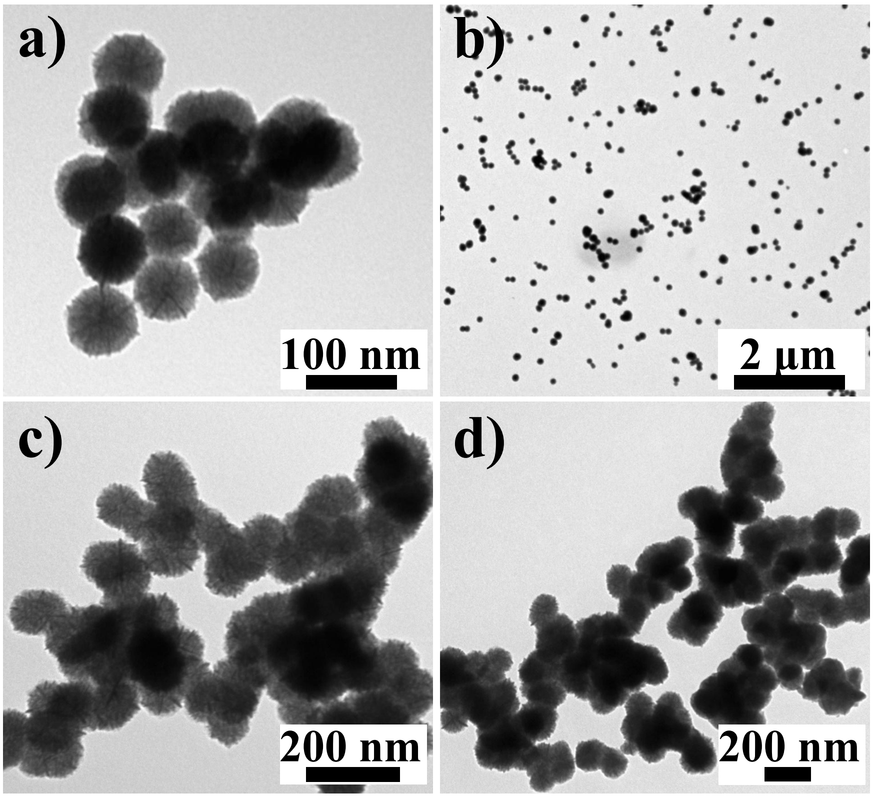


Fig. S5. The effect of different temperatures in the preparation process of C-MnCo(1:3): a,b) room temperature (reacted with 6 h); c) 60 °C (reacted with 30 min) and d) 80 °C (reacted with 30 min).

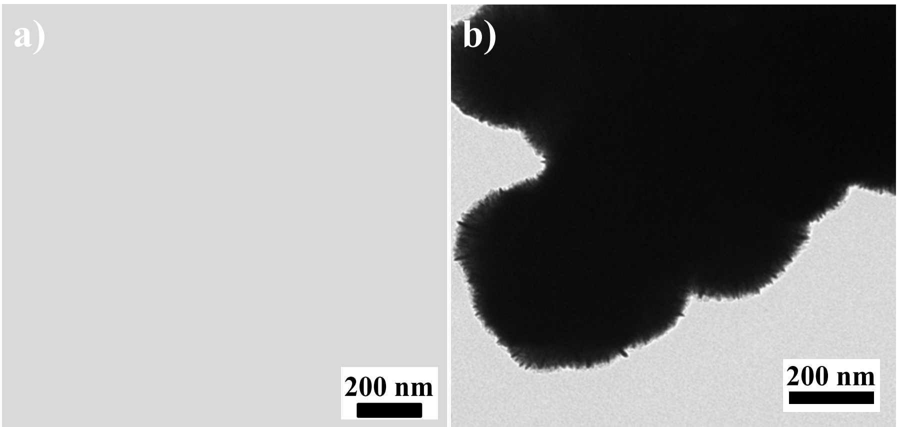


Fig. S6. The TEM images of different concentration for $Mn_xCo_{3-x}O_4$ materials: a) $C_{KMnO4} = 6.25 \times 10^{-3}$ M which was a typical concentration described in the experimental section, b) $C_{KMnO4} = 12.5 \times 10^{-3}$ M.

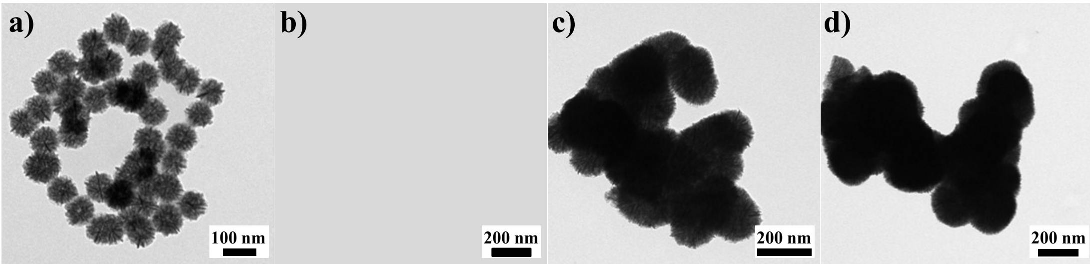


Fig. S7. TEM images about the as-synthesized $Mn_xCo_{3-x}O_4$ materials at different feeding ratio (a) 1:1, (b) 1:3, (c) 1:5 and (d) 1:10.

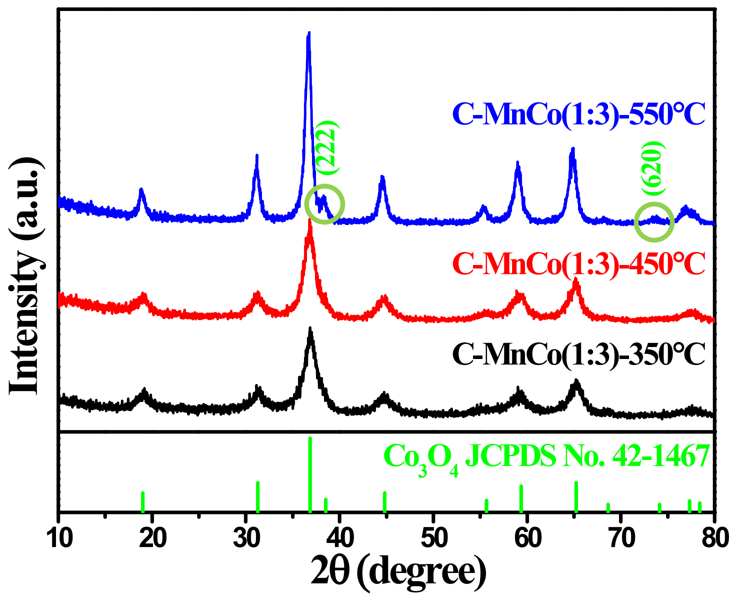


Fig. S8. XRD patterns of MnCo(1:3) after calcination at 350, 450 and 550 °C in air with a ramping speed of 5 °C/min.

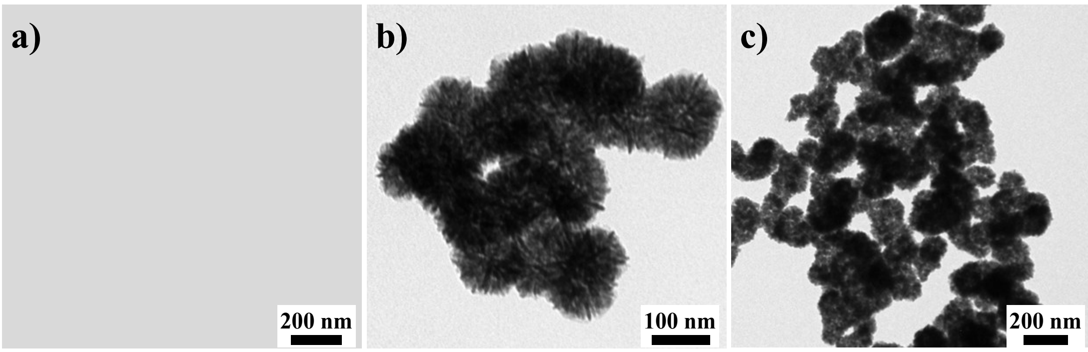


Fig. S9. TEM images of MnCo(1:3) after calcination at 350 ℃ (a), 450 ℃ (b) and 550 ℃ (c) in air at a ramping rate of 5 ℃/min.

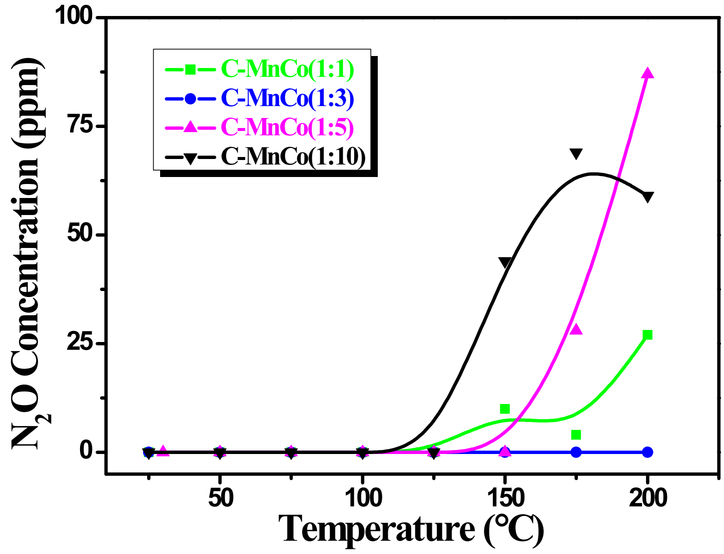


Fig. S10. N_2O concentration detected at different temperature over different $Mn_xCo_{3-x}O_4$ catalysts.

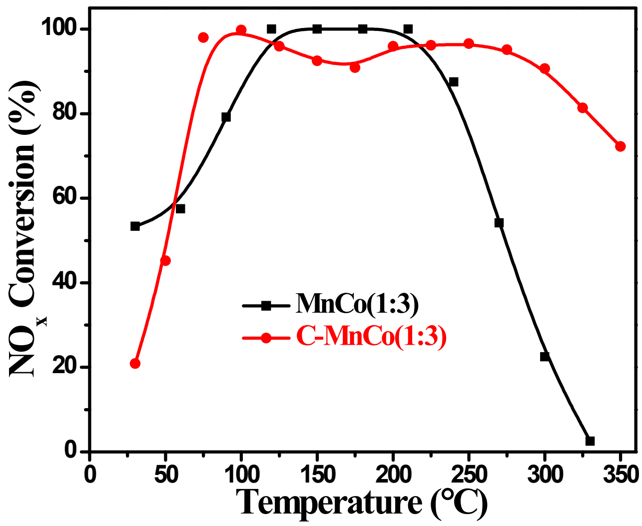


Fig. S11. NH_3-SCR activity of MnCo(1:3) and C-MnCo(1:3).

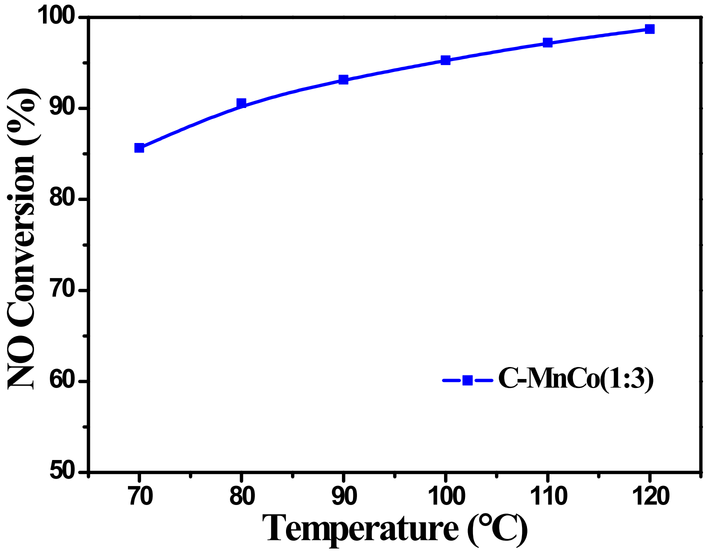


Fig. S12. NH_3-SCR activity from 70 to 120 °C (keep 60 min after reaching each temperature step).

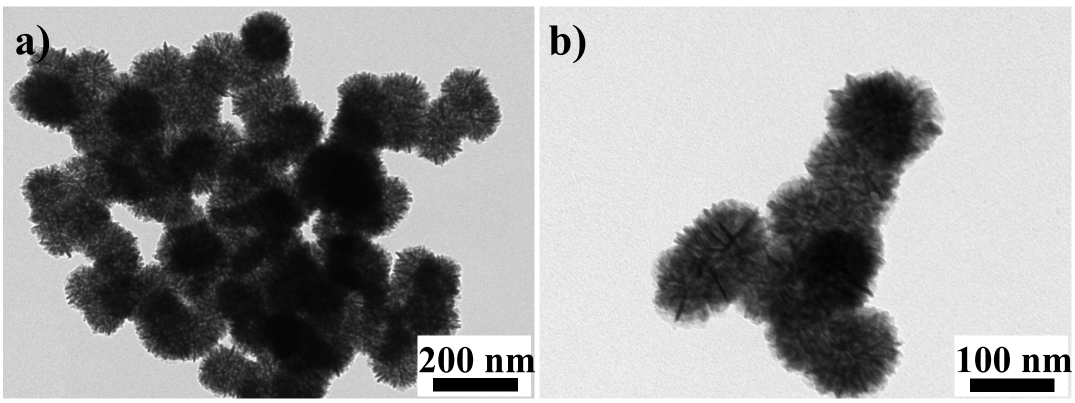


Fig. S13. a, b) The TEM images of C-MnCo(1:3) catalysts after H_2O resistance test.

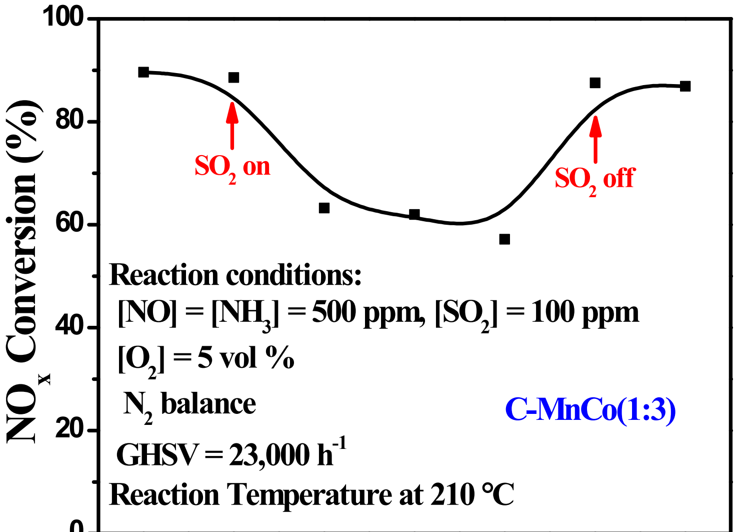


Fig. S14. SO_2 resistance test of C-MnCo(1:3) catalysts at 210 ℃

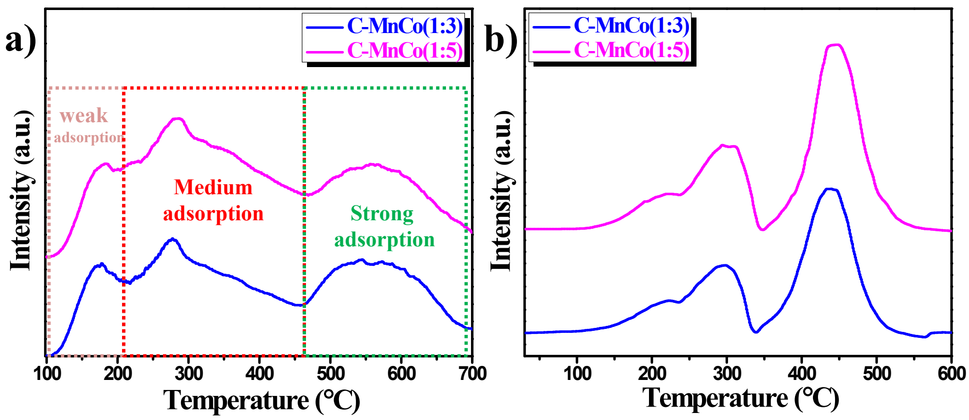


Fig. S15. NH_3-TPD plots (a) and H_2-TPR plots (b) of C-MnCo(1:3) and C-MnCo(1:5) catalysts, respectively.

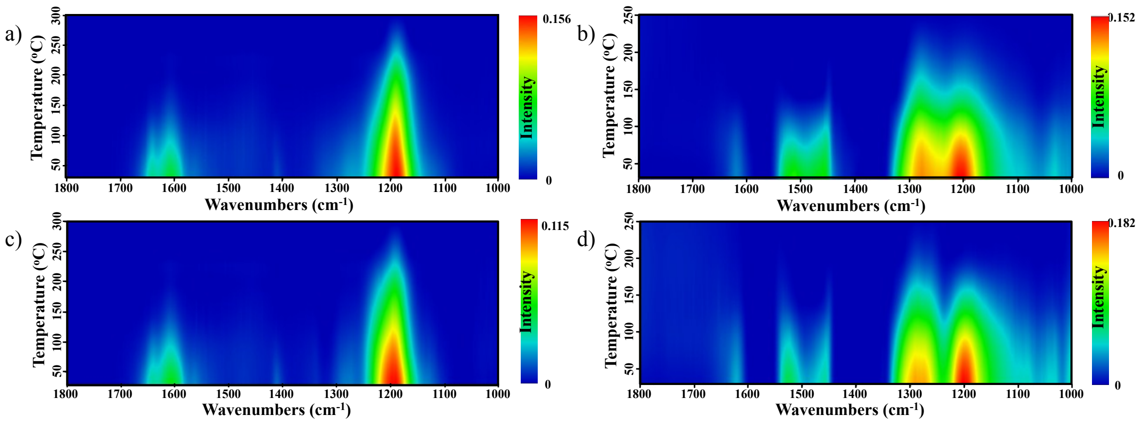
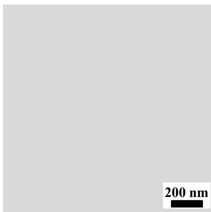
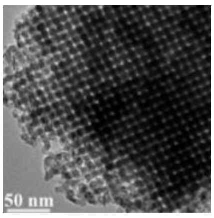
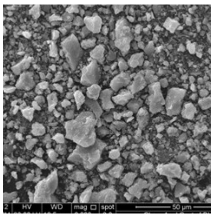
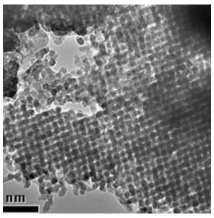
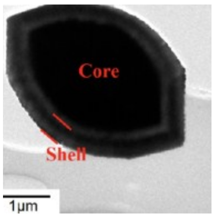
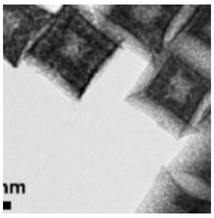
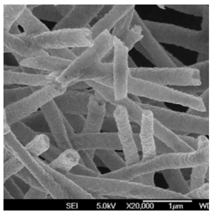
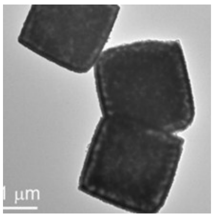


Fig. S16. In situ DRIFT spectra of NH_3 desorption after 500 ppm of NH_3 adsorption for 60 min on C-MnCo(1:3) (a) and C-MnCo(1:5) catalysts (c); In situ DRIFT spectra of NO_x desorption after 500 ppm of NO + 5% O_2 co-adsorption for 60 min on C-MnCo(1:3) (b) and C-MnCo(1:5) catalysts (d) as a function of temperature.

Table S1. Summarized specific information about different preparation procedure.

Sample	Preparation method	BET surface area (m^2/g)	T(S)EM images	Ref.
C-MnCo(1:3)	**Redox, 70 °C，30 min**	**226.7 (before calcination)** **124.0 (after calcination)**		**This work**
$MnCo_2O_4$	**Template-assisted (KIT-6)**	**133**		**[1]**

CoMn(3/1)-CA	**Citric acid, 2 h**	**92**		**[2]**
3D-$MnCo_2O_4$	**Template-assisted (KIT-6, SBA-15)**	**92.9**		**[3]**
Core-shell $MnCo_2O_4$	**Hydrothermal，180 °C，12 h**	**53**		**[4]**
$Mn_xCo_{3-x}O_4$ nanocages	**Self-assemble methods, PVP, 24 h**	**77.1**		**[5]**
$CoMn_2O_4$ hollow nanofibers	**Electrospinning**	**28.8**		**[6]**
$CoMn_2O_4$ hollow microcubes	**Co-precipitation, $Co(NO_3)_2$, $MnSO_4$, ethanol,$(NH_4)_2SO_4$, NH_4HCO_3, 50 °C, 9 h**	**11.4**		**[7]**

References：

[1] C. Xiao, X. Zhang, T. Mendes, G. P. Knowles, A. Chaffee, D. R. MacFarlane, J. Phys. Chem. C 120 (2016) 23976-23983.

[2] C. Shi, Y. Wang, A. Zhu, B. Chen, C. Au, Catal. Commun. 28 (2012) 18-22.

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[4] G. Huang, S. Xu, Z. Xu, H. Sun, L. Li, ACS Appl. Mater. Inter. 6 (2014) 21325-21334.

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[6] G. Yang, X. Xu, W. Yan, H. Yang, S. Ding, Electrochim. Acta 137 (2014) 462-469.

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Table S2. Theoretical weight loss according to the reaction equations.

Items	Reaction equation	Weight loss (%)
1	$12MnO_2 + 36CoOOH \rightarrow 4Mn_3Co_9O_{16} + 18H_2O + 7O_2$	12.6
2	$12Mn(OH)_4 + 36CoOOH \rightarrow 4Mn_3Co_9O_{16} + 42H_2O + 7O_2$	20.5
3	$12MnO_2 + 36Co(OH)_3 \rightarrow 4Mn_3Co_9O_{16} + 54H_2O + 7O_2$	23.9
4	$12Mn(OH)_4 + 36Co(OH)_3 \rightarrow 4Mn_3Co_9O_{16} + 78H_2O + 7O_2$	29.9

The corresponding weight loss from 200 to 350 °C in TG was calculated below:

Weight $_{200\ °C}$ = 92.3%

Weight $_{350\ °C}$ = 82.9%

$$\text{Weight loss}_{200-350\ °C} = \frac{92.3\% - 82.9\%}{92.3\%} \times 100\% = 10.2\%$$

Table S3. The SCR activity about $Mn_xCo_{3-x}O_4$ catalysts from different literatures.

Catalyst	SCR performance (NO conversion > 80%)	GHSV (h^{-1})	BET surface area (m^2/g)	Ref.
C-MnCo(1:3)	75 – 325 °C	23,000		
	100 – 315 °C	45,000	124.0	This work
	115 – 315 °C	90,000		
$MnCo_2O_x$	>80 °C	12,000	42	[1]
$Mn_2Co_1O_x$(combustion)	>125 °C	30,000	63.9	[2]
3D-$MnCo_2O_4$	75 - 300 °C	32,000	92.9	[3]
$Mn_xCo_{3-x}O_4$ nanocages	>125 °C	38,000	77.1	[4]
$CoMn_2O_4$ microspheres	150 – 375 °C	50,000	36	[5]
$Mn_{0.05}Co_{0.95}O_x$	150 - 210°C	60,000	31.9	[6]
$CoMn_2O_4$ spinels	>325 °C	90,000	109	[7]

References：

[1] T. Xu, C. Wang, X. Wu, B. Zhao, Z. Chen, D. Weng, RSC Adv. 6 (2016) 97004-97011.

[2] J. Qiao, N. Wang, Z. Wang, W. Sun, K. Sun, Catal. Commun. 72 (2015) 111-115.

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Calculation

The Nerst equations were described as follows:

$$MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O \quad (1)$$

$$\varphi = \varphi^\theta + \frac{RT}{nF}\ln\frac{oxidant}{reductant} = 1.69 + \frac{0.0591}{3}\lg\frac{[MnO4 -][H +]4}{[MnO2]}$$

$$= 1.69 - \frac{0.0591}{3} \times 4 \times 5.7 = +\ 1.24\ V\ (pH = 5.7,\ T = 298\ K)$$

$$CoOOH + 3H^+ + e^- \rightarrow Co^{2+} + 2H_2O \quad (2)$$

$$\varphi = \varphi^\theta + \frac{RT}{nF}\ln\frac{oxidant}{reductant} = 1.81 + 0.0591\lg\frac{[CoOOH][H +]3}{[Co2 +]}$$

$$= 1.81 - 0.0591 \times 3 \times 5.4 = +\ 0.85\ V\ (pH = 5.4,\ T = 298\ K)$$