

Lattice Distortion in $\text{Co}_3\text{O}_4/\text{Mn}_3\text{O}_4$ Guided Synthesis via Carbon Nanotubes for Efficient Lean Methane Combustion

Xinfang Wei^{1,*}, Ke Yang¹, Qinghan Zhu¹, Jinlong Li¹, Jian Qi^{2,3*}, Haiwang Wang^{1,*}

¹Key Laboratory of Dielectric and Electrolyte Functional Material Hebei Province, Northeastern University at Qinhuangdao, Qinhuangdao 066004, China.

²State Key Laboratory of Biochemical Engineering, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, China.

³School of Chemical Engineering, University of Chinese Academy of Sciences, Beijing 100049, China.

*Correspondence: weixinfang@neuq.edu.cn (X. Wei); jqi@ipe.ac.cn (J. Qi); whwdwdx@neuq.edu.cn (H. Wang).

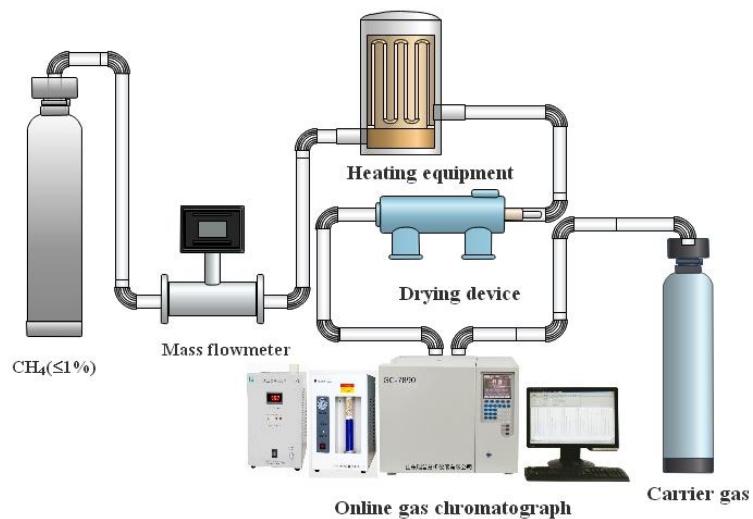


Figure S1. Schematic diagram of the experimental set-up.

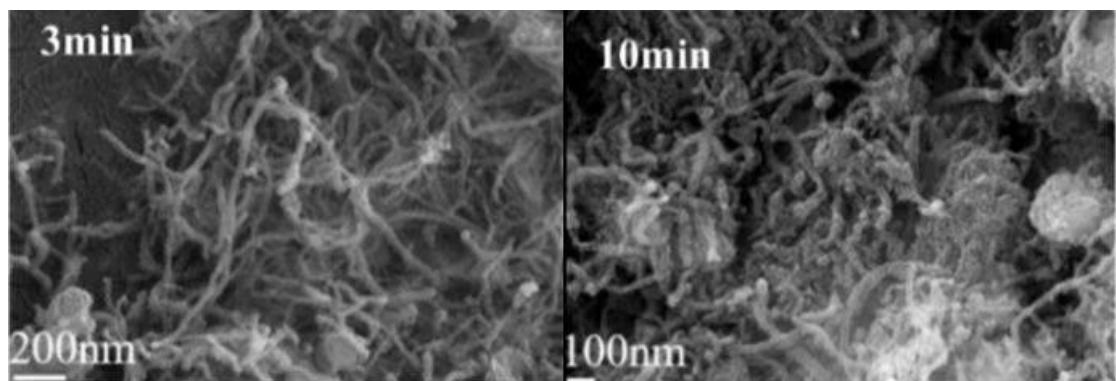


Figure S2. SEM images of Co_3O_4 nano-sheet prepared at annealing times of 3 and 10 min.

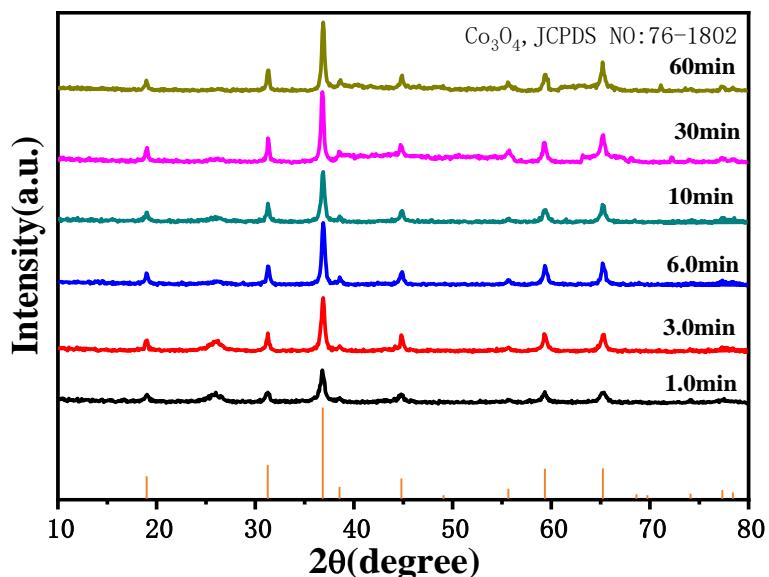


Figure S3. XRD patterns of Co_3O_4 nano-sheet prepared at different annealing times, and JCPDS card is from ref. 50 in the main text.

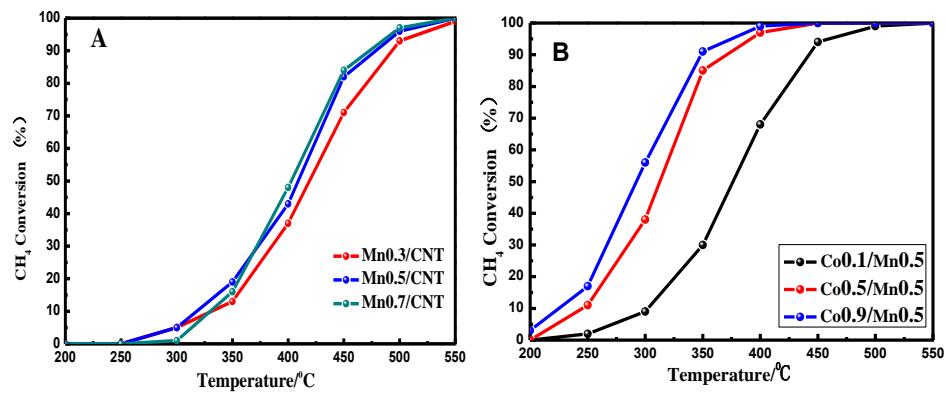


Figure S4. CH₄ conversion from 200 to 550 °C over MnO₂/CNT and Co₃O₄/Mn₃O₄ catalysts.

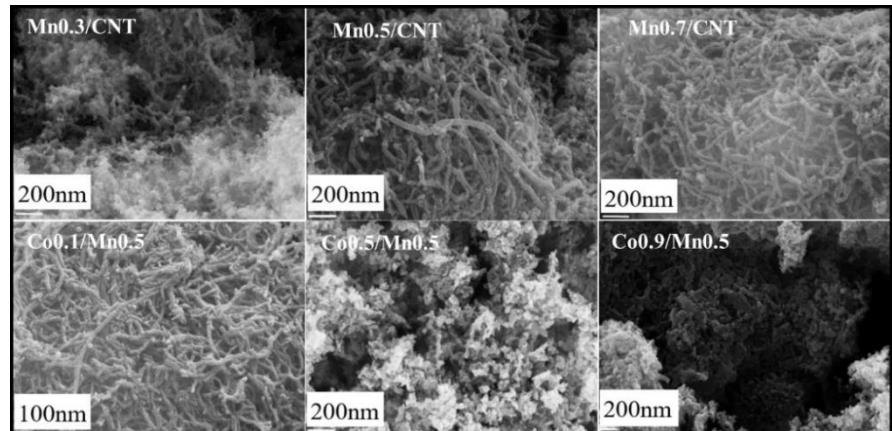


Figure S5. SEM images of MnO₂/CNT and Co₃O₄/Mn₃O₄ catalysts.

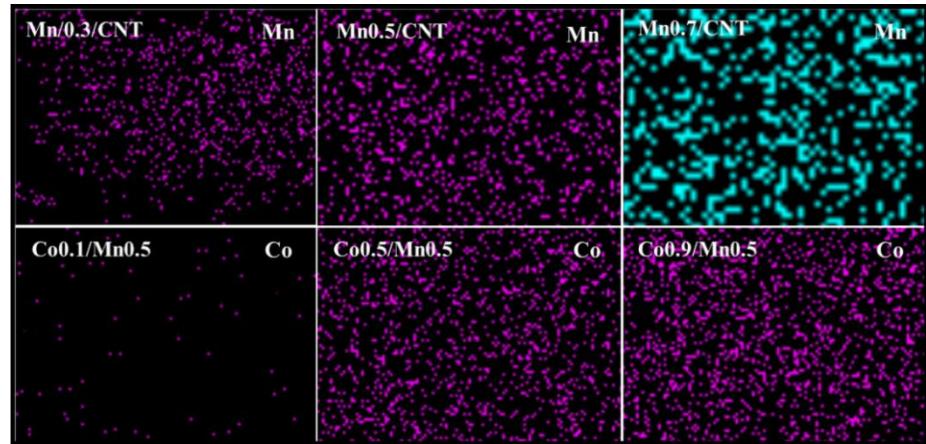


Figure S6. EDS images of MnO_2/CNT and $\text{Co}_3\text{O}_4/\text{Mn}_3\text{O}_4$ catalysts.

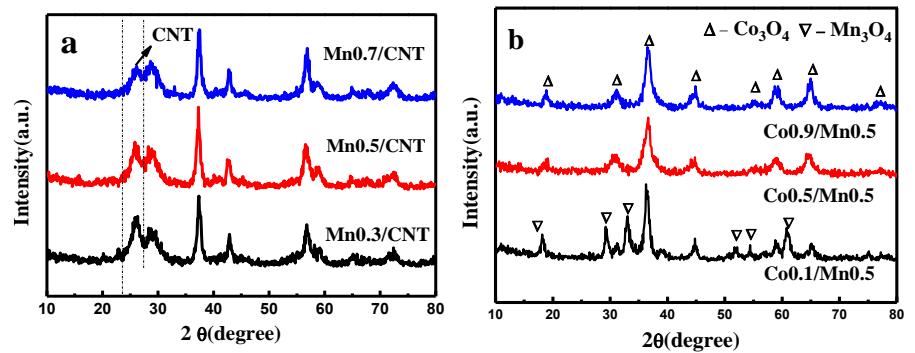


Figure S7. XRD patterns of MnO_2/CNT (a) and $\text{Co}_3\text{O}_4/\text{Mn}_3\text{O}_4$ catalysts (b).

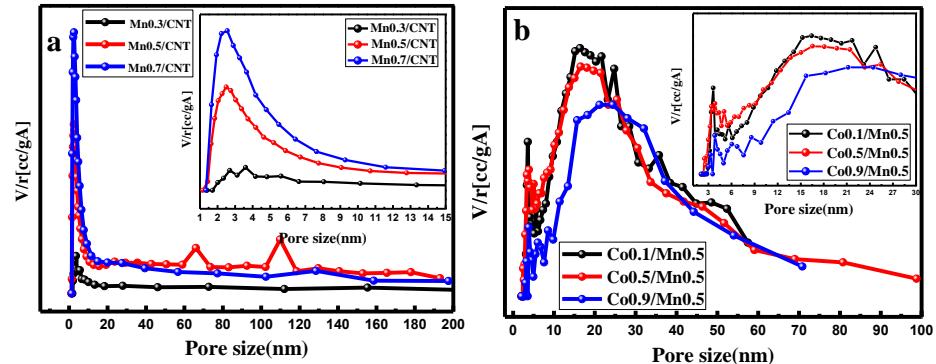


Figure S8. Pore size distributions of MnO_2/CNT (a) and $\text{Co}_3\text{O}_4/\text{Mn}_3\text{O}_4$ catalysts (b).

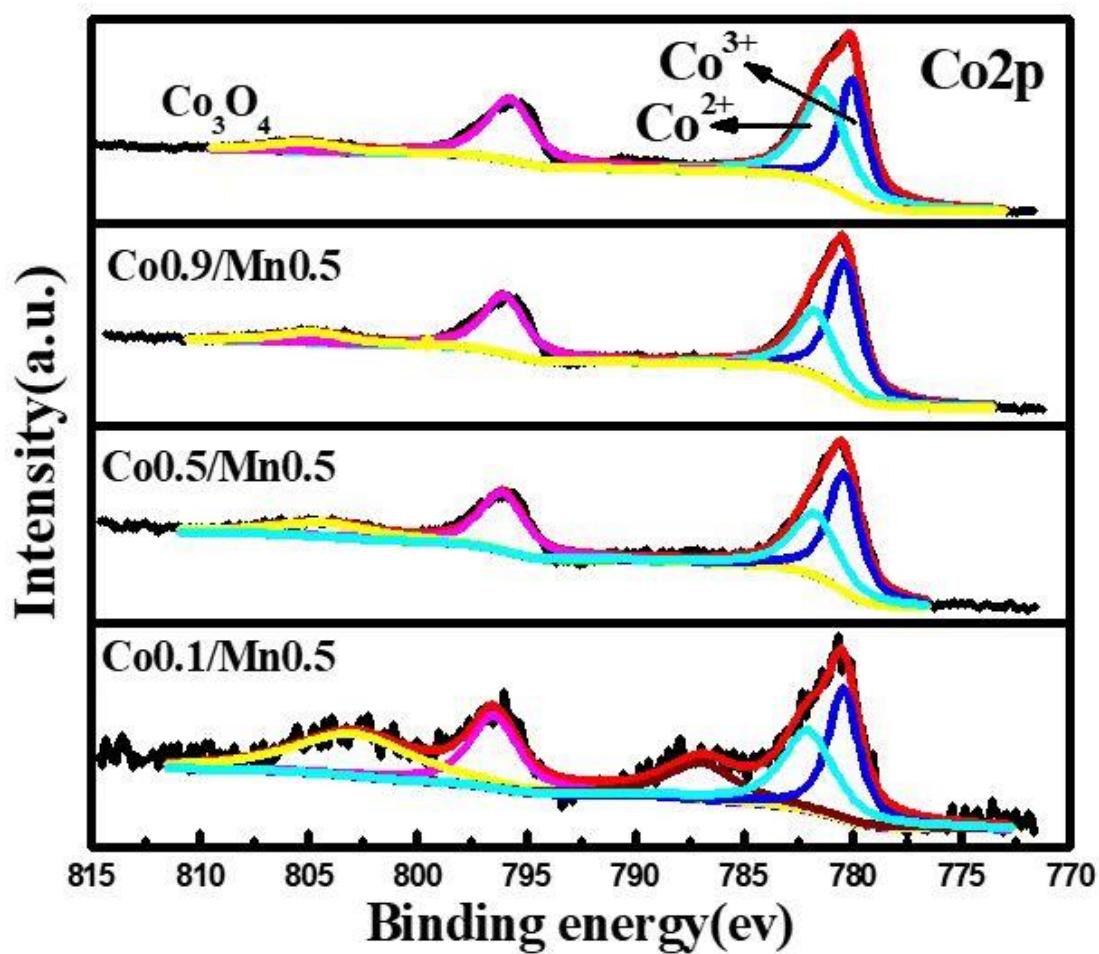


Figure S9. XPS spectra of $\text{Co}^{3+}/\text{Co}^{2+}$ on the surface of $\text{Co}_3\text{O}_4/\text{Mn}_3\text{O}_4$ nano-sheet catalyst with different cobalt-manganese ratios.

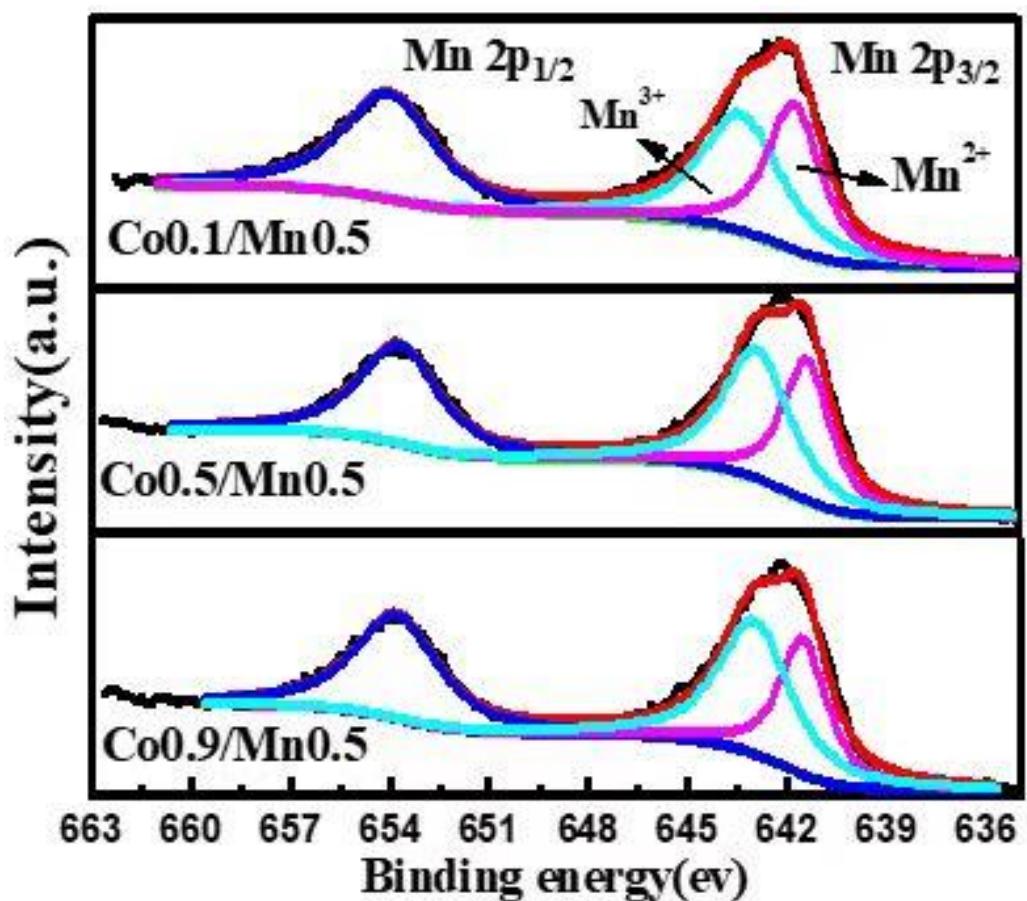


Figure S10. XPS spectra of Mn³⁺/Mn²⁺ on the surface of Co₃O₄/Mn₃O₄ nano-sheet catalyst with different cobalt-manganese ratios.

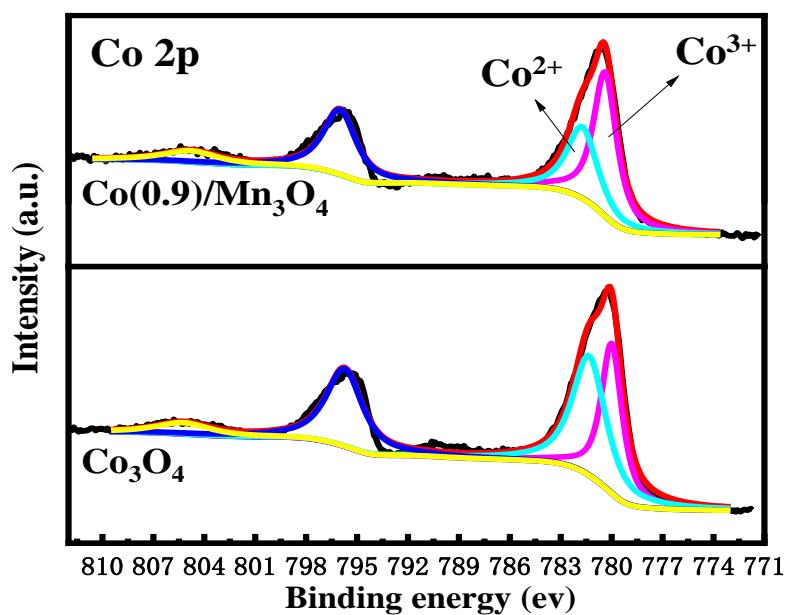


Figure S11. XPS spectra of Co_3O_4 and Co0.9/Mn0.5 nano-catalysts.

According to XPS calculation from Figure S11, the $\text{Co}^{3+}/\text{Co}^{2+}$ ratios of Co_3O_4 and Co0.9/Mn0.5 nano-catalysts were found to be 0.79 and 1.55, respectively. Therefore, the doping of Mn can lead to an increase in the $\text{Co}^{3+}/\text{Co}^{2+}$ ratio of Co0.9/Mn0.5 nanosheets, thereby increasing the migration rate of active oxygen and improving the catalytic activity.

Table S1. Pore parameters of the materials.

Sample	Average Pore Size (nm)	Surface Area (m^2g^{-1})	Total Pore Volume (cm^3g^{-1})
Mn0.3/CNT	29.86	144.18	0.91
Mn0.7/CNT	20.48	170.53	0.63
Co0.1/Mn0.5	35.88	39.37	0.35
Co0.5/Mn0.5	27.06	62.58	0.39

Table S2. Crystal face index, full width at half maximum, and grain size of CNT and Co_3O_4 nanosheet catalysts prepared at different annealing times at 1 min, 6 min, 30 min, and 60 min.

Time/min	hkl	FWHM	D/ \AA
1	(111)	0.782	104
	(220)	0.763	109
	(311)	1.158	73
	(400)	0.736	118
	(511)	0.918	100
	(440)	1.013	93
6	(111)	0.761	107
	(220)	1.313	63
	(311)	1.131	74
	(400)	0.761	114
	(511)	0.976	94
	(440)	0.982	96
30	(111)	0.748	109
	(220)	1.016	82
	(311)	0.903	93
	(400)	0.725	120
	(511)	0.908	101
	(440)	0.946	100
60	(111)	0.601	136
	(220)	0.652	128
	(311)	0.834	101
	(400)	0.793	109
	(511)	0.861	107
	(440)	1.144	83