

Supporting information

Exposed Metal Oxide Active Sites on Mesoporous Titania Channels: a Promising Design for Low-Temperature Selective Catalytic Reduction of NO with NH₃

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1. EXPERIMENT

1.1 Chemicals

Titanium butoxide ($\text{Ti}(\text{OBu})_4$) and Pluronic F127 ($\text{PEO}_{106}\text{PPO}_{70}\text{PEO}_{106}$, $M_w = 12600$) were purchased from Sigma-Aldrich. Ethanol, concentrated HCl (36.5 wt %), acetic acid, copper nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$), and manganese nitrate tetrahydrate ($\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$) were obtained from Shanghai Chemical Corp. All the chemicals were used as received without further purification. Millipore water was used in all the experiments.

1.2 Synthesis of ordered mesoporous CuO/MnO_2 -m TiO_2

Ordered mesoporous titania supported CuO and MnO_2 catalysts were synthesized through an acetic acid-assisted solvent evaporation-induced self-assembly (EISA) strategy by using titanium butoxide, copper nitrate and manganese nitrate as metal oxide precursors, commercial triblock copolymer Pluronic F127 as a template, concentrated HCl as the catalyst, acetic acid as the chelating agent and ethanol as the solvent. A typical synthesis ($0.4\text{CuO}-\text{MnO}_2-10\text{TiO}_2$) procedure is as follows: 1.6 g of F127, 2.4 g of acetic acid, 0.44 g of HCl, 0.097 g of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (0.4 mmol), 0.25 g of $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (1.0 mmol), and 3.4 g of $\text{Ti}(\text{OBu})_4$ (10 mmol) were dissolved in 30 mL of ethanol. The mixture was stirred vigorously for 1 h and casted on Petri dishes for evaporation of solvent. The Petri dishes were placed in an oven at 40 °C for 12 h, followed with heating at 65 °C for 24 h for aging the composites. The composite film was scratched and ground as-made sample was calcined at 350 °C in air for 5 h (ramp rate 2 °C/min) and then ground into powders before the tests of the catalytic reaction. The obtained samples were assigned to $0.4\text{CuO}-\text{MnO}_2-x\text{TiO}_2$, where x represents the atomic ratio of Ti and Mn in the catalyst.

1.3 Catalytic experiments

The catalytic activity measurements for selective catalytic reduction (SCR) of NO by NH_3 were carried out at atmospheric pressure in a fixed bed continuous flow stainless steel reactor located in a tubular furnace. Catalysts (0.5 g) were placed in the reactor. The feed gas composition was as follows: 1000 ppm NO, 1000 ppm NH_3 , 5% O_2 , and N_2 as balance. The gas hourly space velocity (GHSV) was controlled from 10000 to 50000 h^{-1} . The composition of the effluent streams was continually measured by continuous gas analyzers (ABB Easyline EL3020 for NO/ NO_2 and N_2O). Experimental data were recorded when a steady state was achieved at each temperature interval. The NO conversion and N_2 selectivity were calculated as follows:

$$\text{NO conversion (\%)} = \frac{[\text{NO}]_{in} - [\text{NO}]_{out}}{[\text{NO}]_{in}} \times 100\% \quad (1)$$

$$\text{N}_2 \text{ selectivity (\%)} = \frac{[\text{NO}]_{in} + [\text{NH}_3]_{in} - [\text{NO}_2]_{out} - 2[\text{N}_2\text{O}]_{out}}{[\text{NO}]_{in} + [\text{NH}_3]_{in}} \times 100\% \quad (2)$$

where, the subscripts in and out indicated the inlet and outlet concentration at steady state, respectively.

1.4 Measurement and Characterization

Small-angle X-ray scattering (SAXS) measurements were taken on a Nanostar U small-angle X-ray scattering system employing Cu K α radiation (40 kV, 35 mA). The d-spacing values were calculated by the formula $d = 2\pi/q$, and the unit cell parameters were calculated with the formula $a = 2d_{100}/\sqrt{3}$. Transmission electron microscopy (TEM) images were collected on a JEOL Model 2011 electron microscope operated at 200 kV. Samples were ground in an agate mortar and dispersed in ethanol for 15 min. And the fine suspension was then deposited on a carbon film supported on a molybdenum grid for measurements. Mapping images were also taken by transmission electron microscopy to analyze the distribution of Cu and Mn with the molybdenum grid. Field-emission scanning electron microscopy (FE-SEM) images were obtained with a Hitachi Model S-4800 microscope and the samples without further gold-spraying treatment were used for observation. High angle annular dark field (HAADF) images and elemental mapping were measured with a spherical aberration corrected scanning transmission electron microscopy (Cs-STEM). N₂ adsorption-desorption isotherms were measured at 77 K with a Micromeritics Tristar 3020 analyzer. Sample was degassed under vacuum at 180 °C for at least 6 h before measurements. The pore size distribution was derived from the adsorption branches of isotherms using the Barrett-Joyner-Halenda (BJH) model. The pore volume was estimated from the adsorbed amount at p/p_0 of 0.995. The specific surface area was calculated based on the Brunauer-Emment-Teller (BET) method. X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advance diffractometer using Cu K α radiation source. X-ray photoelectron spectroscopy (XPS) was recorded by a Perkin Elmer PHI5000C spectroscope with a Mg K α line as the excitation source. Temperature-programmed reduction by hydrogen (H₂-TPR) was performed on a Micromeritics analyzer. Sample was degassed at 250 °C under N₂ flow for 1 h. After cooling to 50 °C, the flowing gas was switched to 10 % H₂/N₂, and the sample was heated to 500 °C at a ramping rate of 10 °C/min. The H₂ consumption was monitored by a TCD. Temperature-programmed desorption experiments of ammonia (NH₃-TPD) were also conducted on the Micromeritics analyzer. Sample was preheated under N₂ flow at 200 °C for 2 h, then saturated with ammonia at 50 °C for 1.5 h and subsequently at the same temperature for 3 h to remove physisorbed ammonia. Finally, the TPD operation was carried out from 50 to 600 °C at a heating rate of 10 °C/min. The amount of NH₃ desorbed was monitored by a TCD.

Table S1. Texture properties of the mesoporous CuO/MnO₂-mTiO₂ composites synthesized by acetic acid-assistant co-assembly approach.

Samples	Pore size ^a (nm)	V _t ^b (cm ³ g ⁻¹)	S _{BET} ^c (m ² g ⁻¹)
pure mesoporous TiO ₂	6.7	0.34	203
0.4CuO-MnO ₂ -10TiO ₂	6.8	0.36	211
0.4CuO-MnO ₂ -20TiO ₂	7.6	0.38	207
0.4CuO-MnO ₂ -50TiO ₂	8.0	0.51	317

^a Pore sizes derived from the adsorption branches of the isotherms by using the BJH method.

^b Total pore volumes estimated based on the volume adsorbed at p/p_0 of ~ 0.995 .

^c BET specific surface area evaluated in p/p_0 from 0.05 to 0.20.

Table S2. The surface atomic concentration of the mesoporous CuO/MnO₂-mTiO₂ composites measured by XPS.

Samples	Atomic concentration (%)			
	Cu	Mn	Ti	Cu: Mn: Ti
0.4CuO-MnO ₂ -10TiO ₂	3.3	14.9	81.8	0.22:1:5.5
0.4CuO-MnO ₂ -20TiO ₂	2.5	11.0	87.4	0.25:1:8.7
0.4CuO-MnO ₂ -50TiO ₂	1.1	4.3	94.6	0.26:1:21.9

Table S3. The atomic concentration of the mesoporous CuO/MnO₂-mTiO₂ composites measured by inductively coupled plasma-atomic emission spectrometry (ICP-AES).

Samples	Atomic concentration (%)			
	Cu	Mn	Ti	Cu: Mn: Ti
0.4CuO-MnO ₂ -10TiO ₂	3.3	8.6	88.2	0.38:1:10.3

0.4CuO-MnO ₂ - 20TiO ₂	1.7	4.5	93.8	0.38:1:20.8
0.4CuO-MnO ₂ - 50TiO ₂	0.33	1.4	98.2	0.23:1:68.8

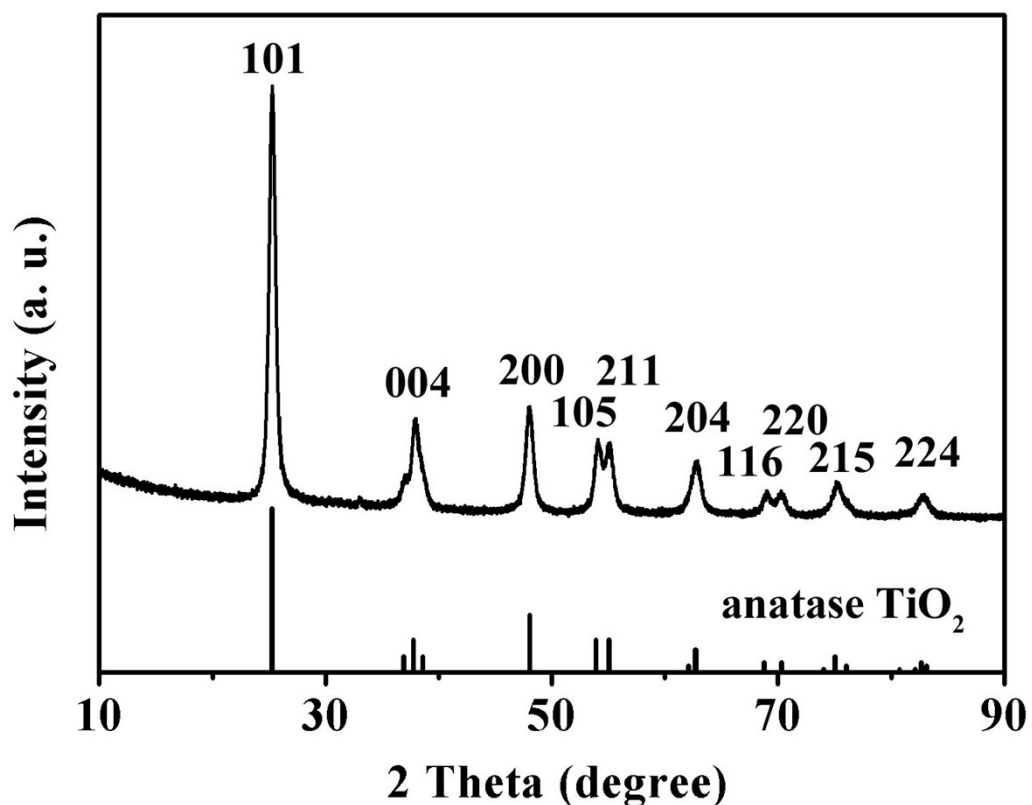


Figure S1. The XRD patterns of the mesoporous 0.4CuO-MnO₂-10TiO₂ composites after calcination at 550 °C in air and standard anatase titanium oxide (JCPDS 21-1272). All the diffraction peaks of the mesoporous 0.4CuO-MnO₂-10TiO₂ composites can be assigned to the pure anatase titanium oxide phase, and no crystalline phase such as copper oxide and manganese oxide was detected under the treatment at such high temperature. These results further confirm that the copper and manganese oxides are highly dispersed on the mesoporous titania matrix.

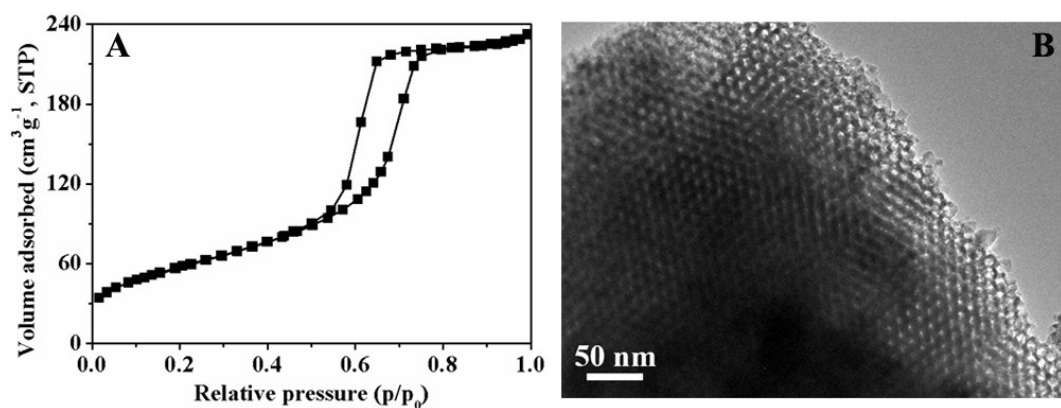


Figure S2. The N₂ adsorption-desorption isotherm curves and TEM image of the mesoporous 0.4CuO-MnO₂-10TiO₂ catalyst (viewed from the [001] direction).

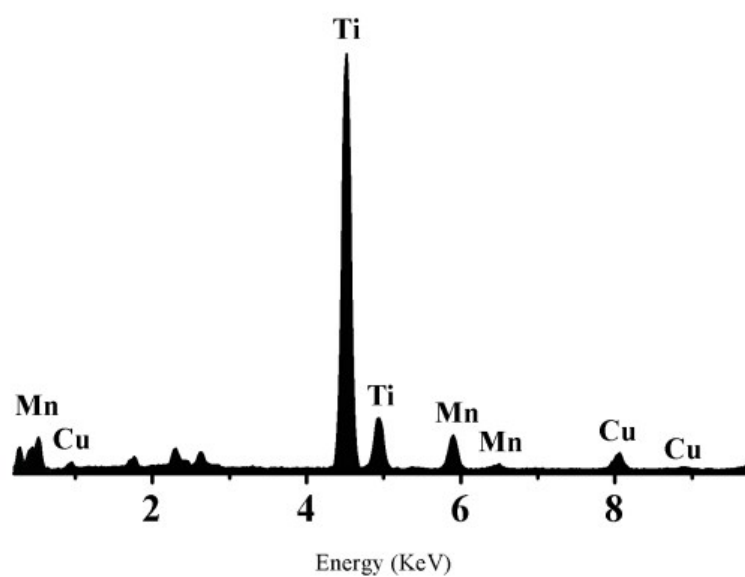


Figure S3. EDX spectrum of the mesoporous 0.4CuO-MnO₂-10TiO₂ catalyst.

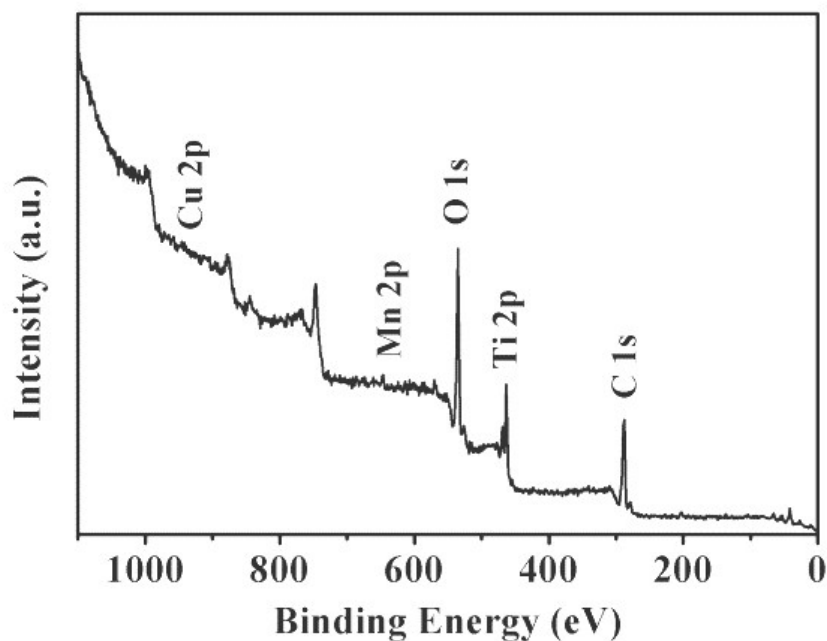


Figure S4. The survey XPS spectrum of the mesoporous 0.4CuO-MnO₂-10TiO₂ catalyst.

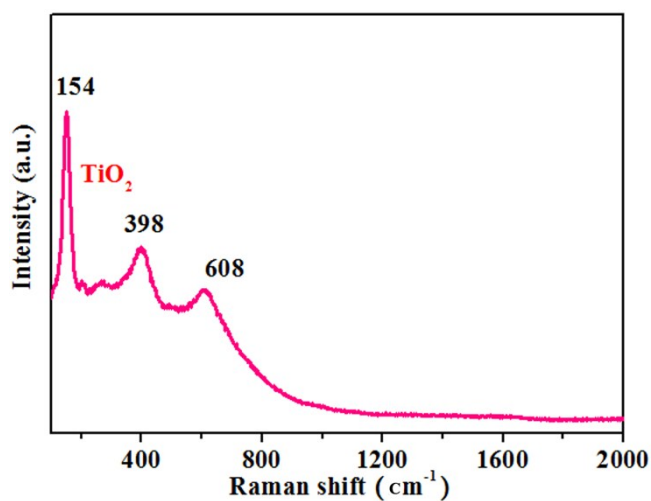


Figure S5. Raman spectrum of mesoporous 0.4CuO-MnO₂-10TiO₂ catalyst. Two bands at 154 and 398 cm⁻¹ are in agreement with the characteristic peaks of anatase TiO₂ phase. The board bands at 608 cm⁻¹ indicates the symmetrical Mn-O vibrations of MnO₂ and small grain size of CuO nanocrystals.

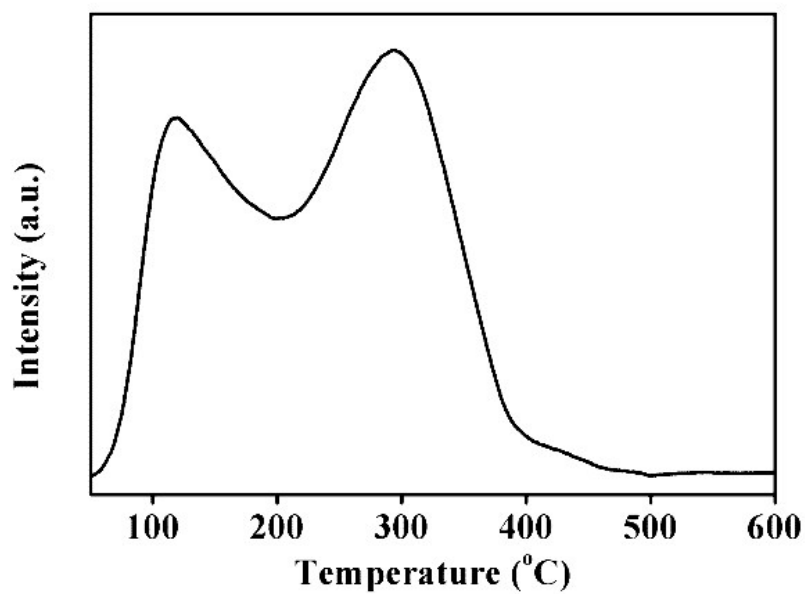


Figure S6. NH₃-TPD profile of the ordered mesoporous 0.4CuO-MnO₂-10TiO₂ catalyst.

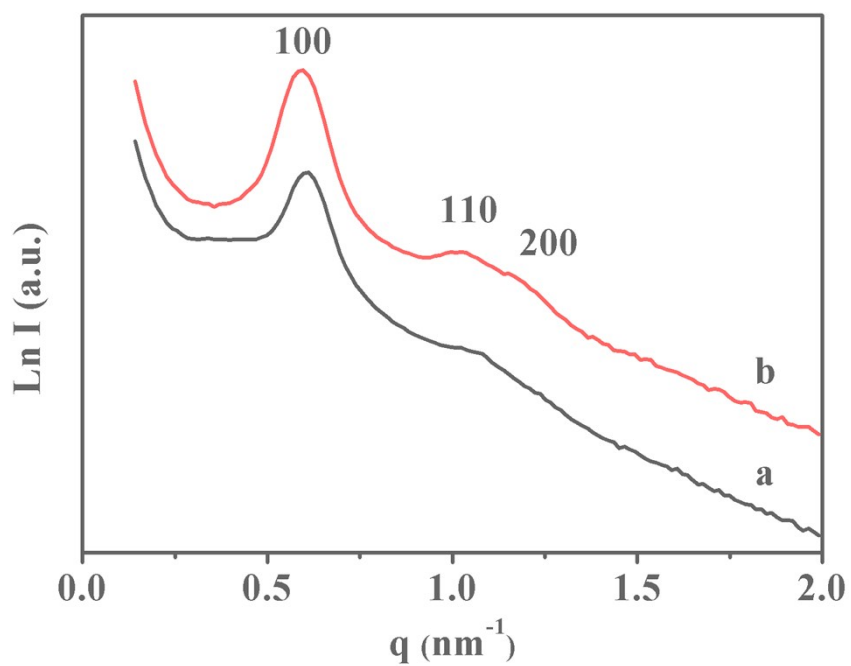


Figure S7. SAXS patterns of the (a) mesoporous 0.4CuO-MnO₂-20TiO₂ and (b) 0.4CuO-MnO₂-50TiO₂ catalyst.

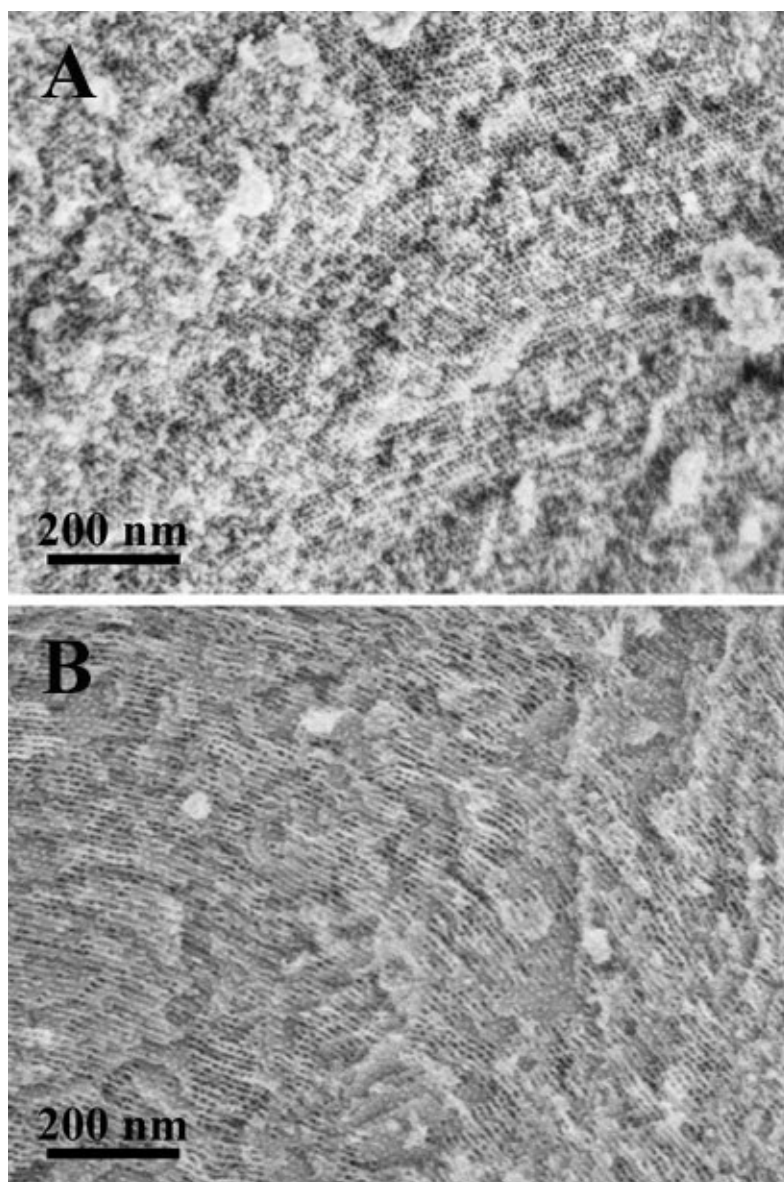


Figure S8. SEM images of the (A) mesoporous $0.4\text{CuO-MnO}_2\text{-}20\text{TiO}_2$ and (B) mesoporous $0.4\text{CuO-MnO}_2\text{-}50\text{TiO}_2$ catalyst.

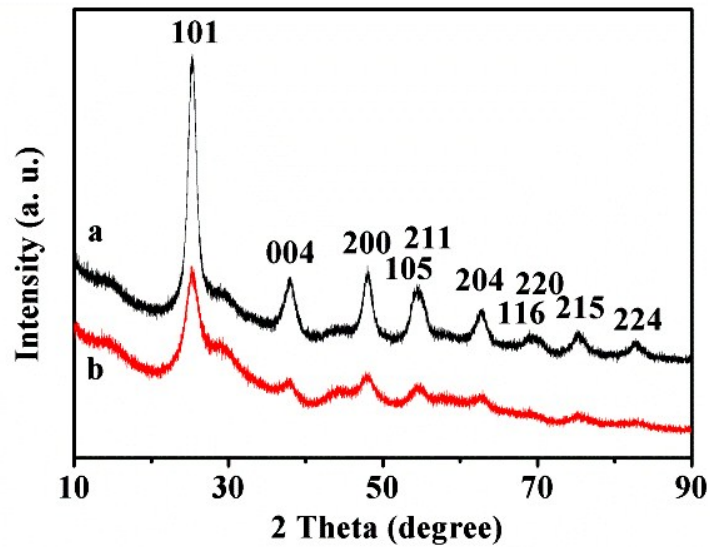


Figure S9. XRD patterns of the (a) mesoporous $0.4\text{CuO-MnO}_2\text{-}20\text{TiO}_2$ and (b) mesoporous $0.4\text{CuO-MnO}_2\text{-}50\text{TiO}_2$ catalyst.

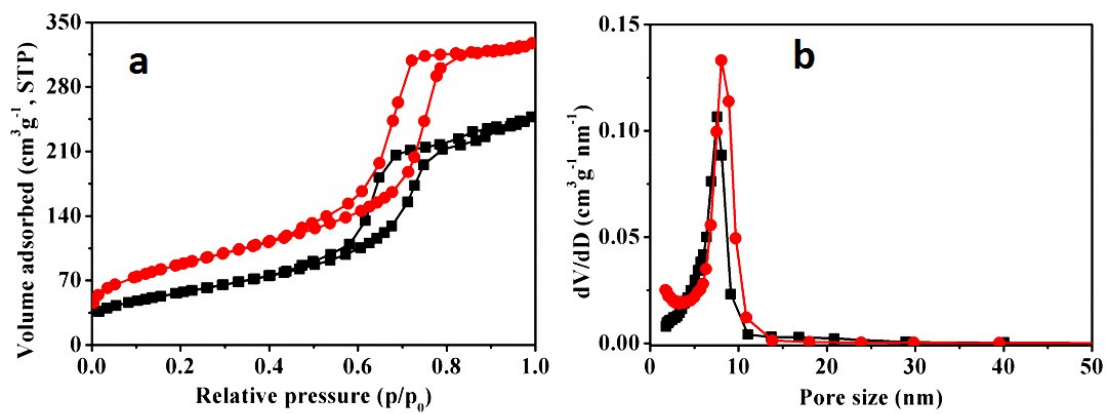


Figure S10. N_2 adsorption-desorption isotherms (a) and pore size distribution plots (b) of the mesoporous $0.4\text{CuO-MnO}_2\text{-}20\text{TiO}_2$ (\blacksquare) and mesoporous $0.4\text{CuO-MnO}_2\text{-}50\text{TiO}_2$ (\bullet) catalyst.

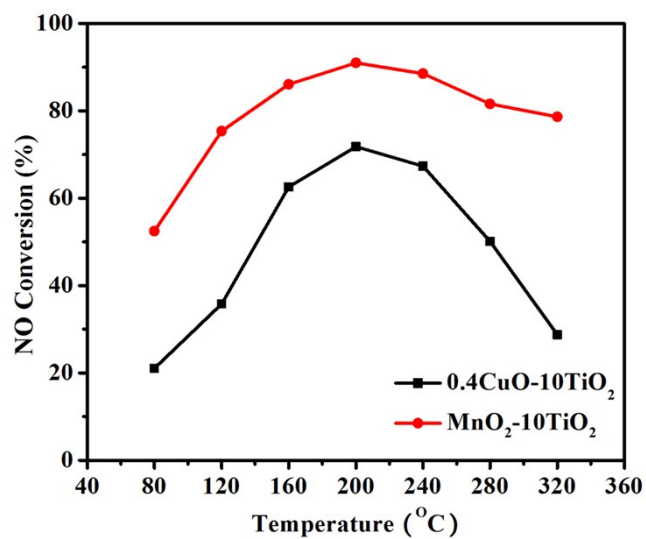


Figure S11. NH₃-SCR performance of the mesoporous 0.4CuO-10TiO₂ and MnO₂-10TiO₂ composites. Reaction conditions: [NO] = [NH₃] = 1000 ppm, [O₂] = 5 vol %, N₂ balance and GHSV = 20000 h⁻¹.