

Supporting information

Two-Step Pyrolysis of Mn MIL-100 MOF into MnO Nanoclusters/Carbon and the Effect of N-doping

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Experimental Section

1. Chemicals

Trimesic acid (95%), $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ($\geq 97\%$), methanol (99.9%), ethanol (99.5%), dicyandiamide (99%) and boron nitride (98 %) were all purchased from Sigma-Aldrich.

2. Synthesis of Mn MIL-100 MOF

Mn MIL-100 was synthesized following Stoke's work with some modifications (composition of the desolvated form of Mn MIL-100 as $[\text{Mn}_3(\text{O})(\text{BTC})_2]$).¹

2 mmol of trimesic acid and $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ was dissolved in 10 mL of *methanol* in a glass vial. The mixture is dissolved and mixed by stirring for 30 mins. The mixture is then transferred into a hydrothermal autoclave liner of 45 ml in volume. The solution was then heat-treated in a sealed stainless steel autoclave at 125 °C for 2 h. After cooling down, a brown color solid is obtained and washed with ethanol for three times. The sample is stored in ethanol.

3. N-doping of the Mn MIL-100 MOF

3 mmol dicyandiamide and 0.5 mmol Mn MIL-100 were mixed in 20 ml methanol and the mixture went through hydrothermal treatment in a 45 ml autoclave liner for various durations at 90 °C. The product is then washed with ethanol for three times.

4. In-situ Studies

Thermogravimetric analysis–mass spectrometry (TG-MS) test of the Mn MIL-100: TG-MS was conducted on a Mettler Toledo thermogravimetric analyzer, coupled with a Pifzer mass spectrometry, which is capable of qualitative analysis of evolved gases during thermal decomposition. Range of mass detected: 1-100 AMU (atomic mass unit). About 6-10 mg of Mn MIL-100 was put in an aluminum pan inside the chamber. Then, the sample was heated to 700 °C at the ramp rate of 5 °C/min in N_2 , flowing at 100 mL/min. N_2 is flushed for 30 min before the heating started. Signals *vf* below AMUs were collected while only the detected ones are shown in the results: 2 (H_2), 16 (CH_4), 17 (NH_3), 18 (H_2O), 28 (N_2), 30 (NO), 32 (O_2), 44 (CO_2), 46 (NO_2), 55(Mn), 78(C_6H_6).

In-situ scanning transmission electron microscopy (STEM) study of the Mn MIL-100's pyrolysis in the STEM chamber: *In-situ* STEM study was conducted on a JEOL ARM200f microscope at an acceleration voltage of 200 kV, using the *in-situ* heating and biasing holder (DENSsolutions) with heating MEMS (Micro-electromechanical system) chips with Si_3N_4 membrane. Powder of Mn MIL-100 was well dispersed in ethanol by ultrasonication, and then dropped onto the chip. The temperature accuracy is within 5%. The base vacuum is about $1\text{E}-7$ mbar.

In-situ XRD study of the Mn MIL-100's pyrolysis in N_2 gas: *In-situ* XRD study was conducted on a PANalytical X'Pert PRO using $\text{Cu K}\alpha$ radiation. Powder of Mn MIL-100 was well dispersed in ethanol by ultrasonication, and then dropped onto a silicon wafer that was placed on the XRD sample holder. The heating cell is vacuumed to $1\text{E}-5$ mbar before N_2 is filled. The sample is being heated up from room temperature to 900 °C with N_2 flowing at 50 mL/min. The volume of the cell is about 100 mL. XRD was tested when the set temperature is reached. Ramp rate of 5°C/min is used and the testing

time at each temperature is about 7 min.

5. Pyrolysis/carbonization of the MOFs

About 60-100 mg of the as-synthesized Mn MIL-100 or the N-doped Mn MIL-100 powder was placed in an alumina crucible. The crucible was then placed in a tube furnace connected with mechanical and turbo pumps. A vacuum level of $\sim 5E-4$ mbar was obtained before filling with N_2 gas to atmospheric pressure. The above degassing/ N_2 -filling cycle was repeated for 3 times. Then, the MOF went through heat-treatment with N_2 flowing at 300 mL/min. Ramp rate of 5 °C/min was used to reach 700 °C and duration of holding at 700 °C is 2 h. The product was retrieved upon cooling down to room temperature. The table below shows the sample nomenclature based on N-doping and heat-treatment conditions.

Table S1. Nomenclature of samples based on N-doping level and heat-treatment.

Sample name	Starting material	Treatment	N at%
N-MOF1	Mn MIL-100	12 h at 90°C	3.5
N-MOF2		18 h at 90°C	4.5
N-MOF3		24 h at 90 °C	6.3
MnO/C			0
MnO/NC1	3.5 at% N-doping	2 hr at 700 °C, N_2	3.1
MnO/NC2	4.5 at% N-doping		4.2
MnO/NC3	6.3 at% N-doping		4.7

6. Characterizations

The as-synthesized Mn MIL-100, N-doped Mn MIL-100 and the carbonized samples were then analyzed using transmission electron microscopy (TEM), X-ray diffraction (XRD), energy dispersive X-ray analysis (EDX), CHNS analyzer, inductively coupled plasma-optical emission spectrometer (ICP-OES). XRD patterns were obtained using a Bruker AXS X-ray powder diffractometer (D8 Advance, Cu $K\alpha$, $\lambda = 0.15418$ nm). Elemental analysis was conducted by using the CHNS (Carbon, Hydrogen, Nitrogen and Sulphur) analyzer (Elementar vario MICRO cube) for carbon, nitrogen and hydrogen contents and ICP-OES (Perkin Elmer Optima 5300DV) for manganese contents. Field-emission scanning electron microscopy (SEM) were conducted using a SUPRA 40 ZEISS. TEM imaging were conducted using a JEOL JEM-2010 microscope under an acceleration voltage of 200 kV. Specific surface area and pore size distribution were calculated from N_2 adsorption/desorption measurement (Micromeritics 3Flex). Thermal gravimetric analysis (TGA) of the Mn MIL-100 was done using a TA Instruments Q500.

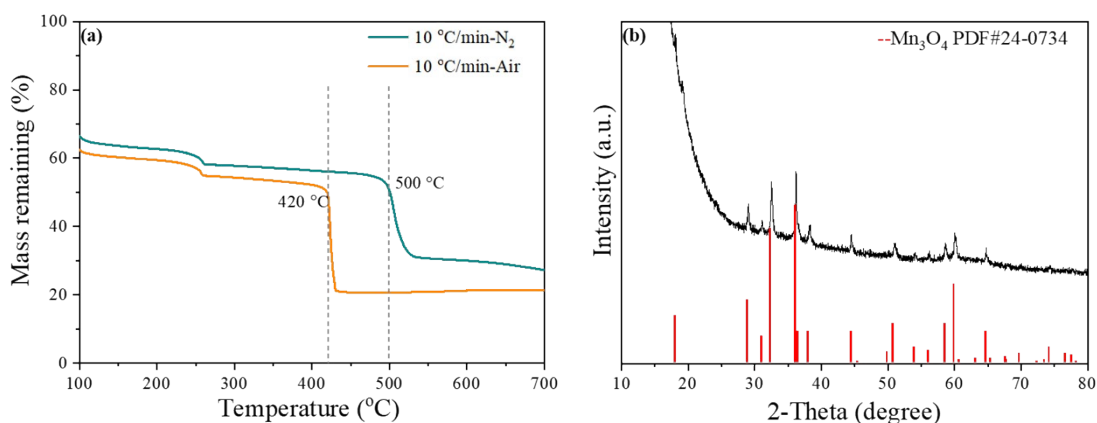


Figure S1. (a) TGA results in air and N₂ with a ramping rate of 10 °C/min and gas flow of 100 mL/min. (b) XRD result of the Mn MIL-100 carbonized in air at 450 °C for 2h.

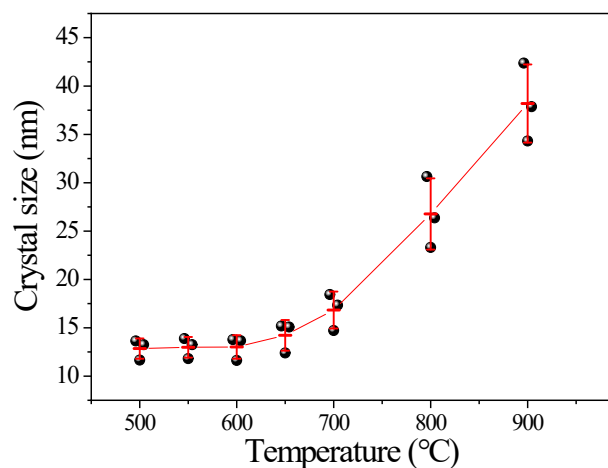


Figure S2. Crystal size calculated from *in-situ* XRD results using Debye-Scherrer's formula, based on the peaks at 34.9, 40.5 and 58.7 degree of 2 theta.

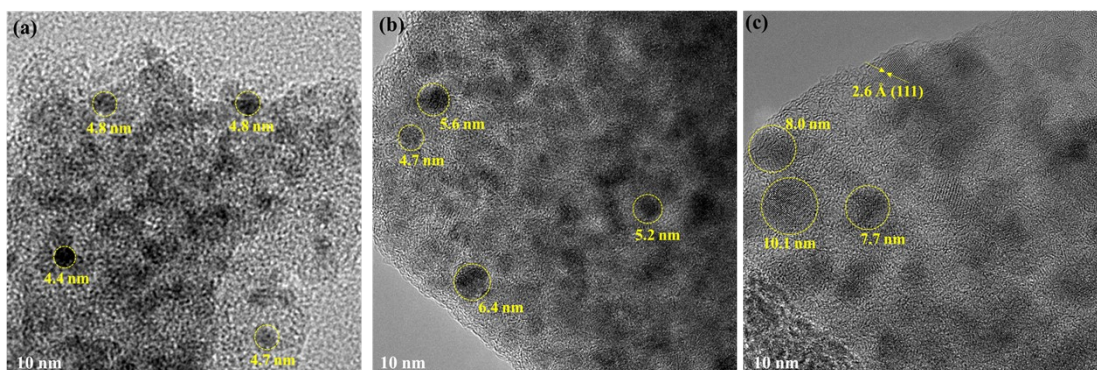


Figure S3. High-resolution TEM images of the Mn MIL-100 pyrolyzed/annealed at a) 700 (Sample MnO/C), b) 800 and c) 900 °C, showing the particle sizes of the MnO nanoparticles and the lattice fringe corresponds to the (111) plan of MnO crystal (PDF

#07-0230).

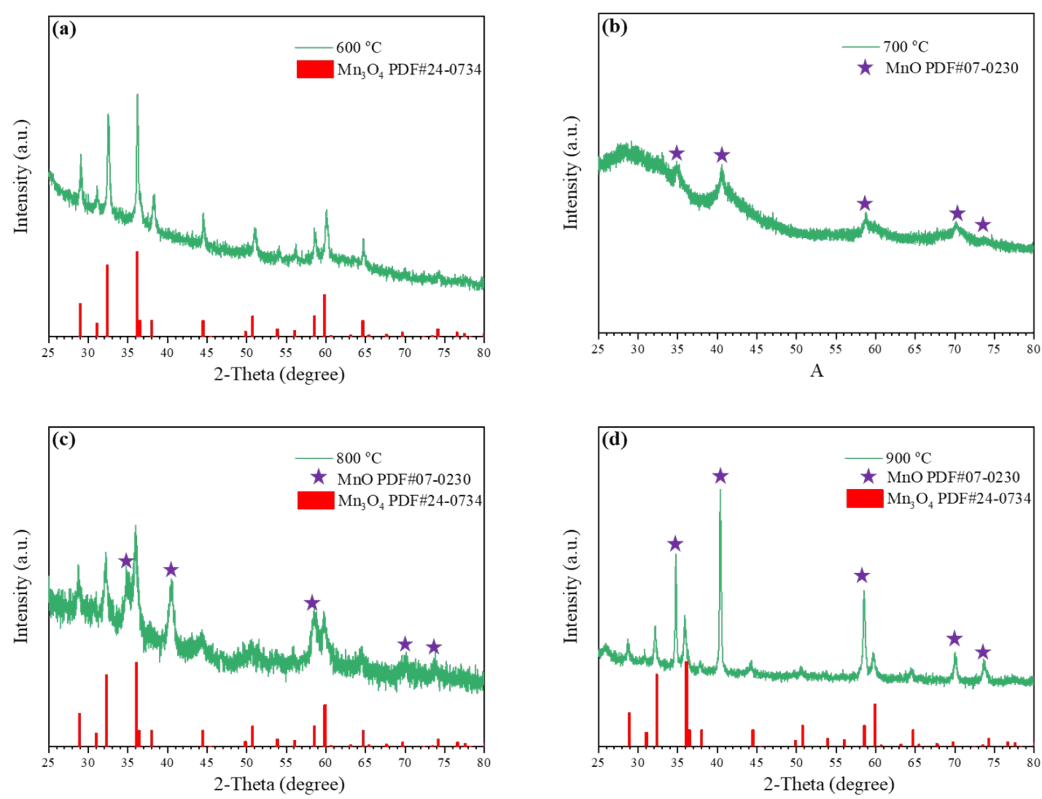
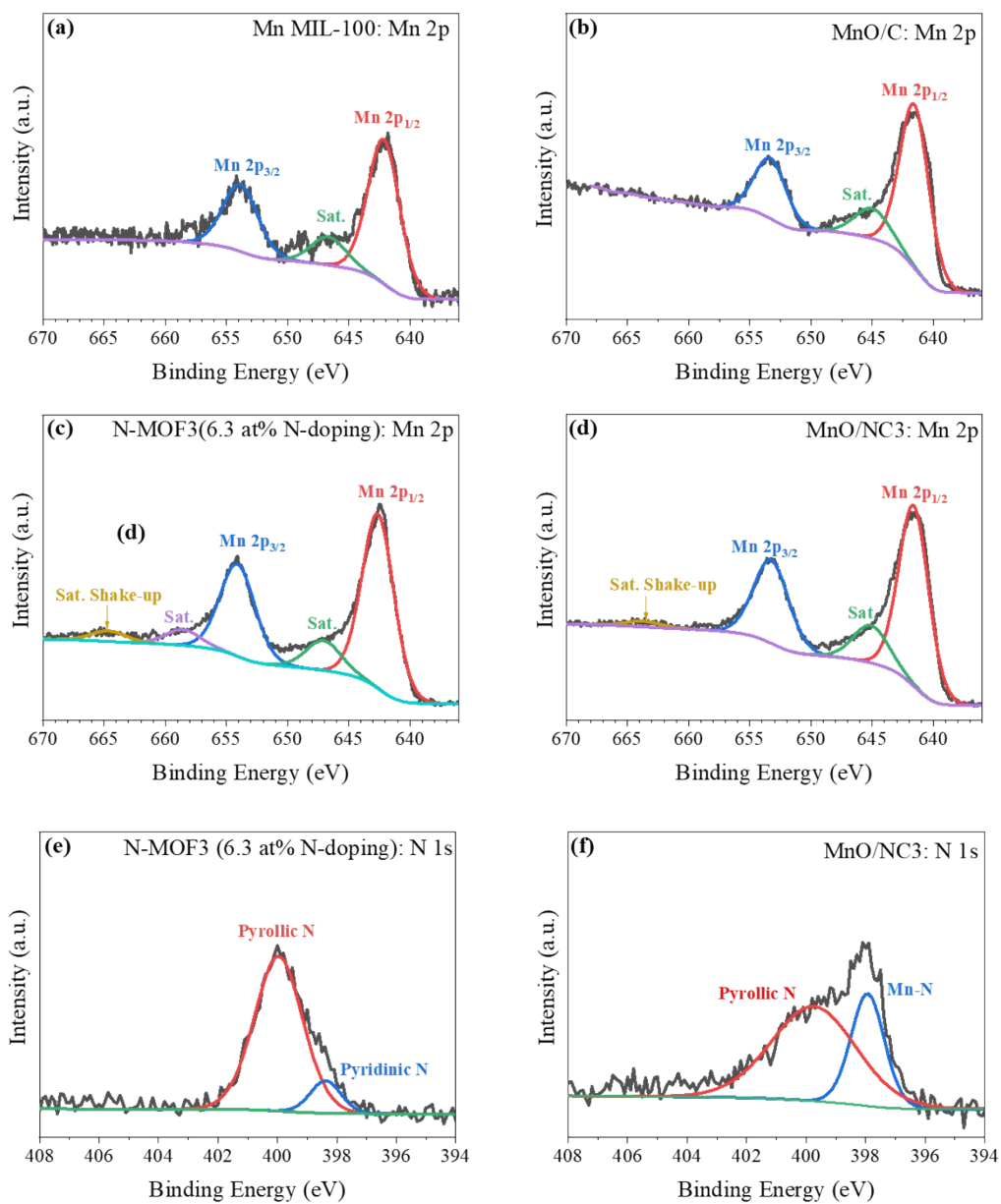


Figure S4. XRD results of the Mn MIL-100 pyrolyzed/annealed at a) 600, b) 700 (Sample MnO/C), c) 800 and d) 900 °C.



Figure

e S5. XPS results of Mn 2p for (a) Mn MIL-100, (b) MnO/C, (c) N-MOF3 and (d) MnO/NC3; N 1s for (e) N-MOF3 and (f) MnO/NC3.

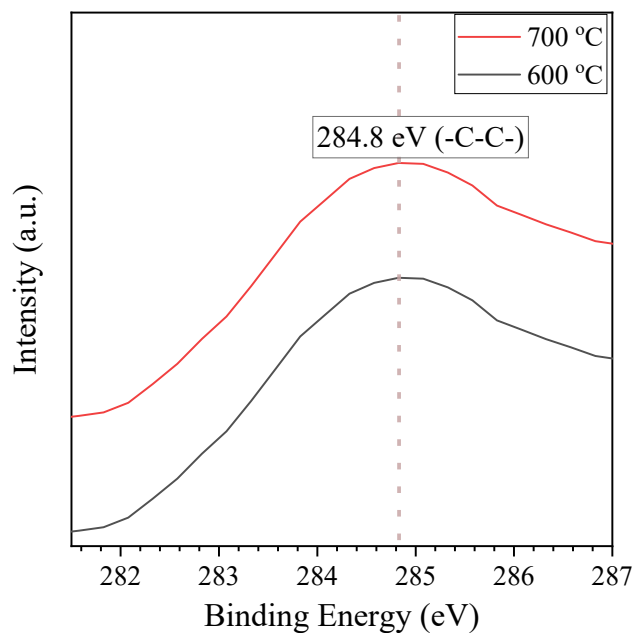


Figure S6. EELS spectrum for carbon 2s during *in-situ* STEM test at 600 and 700 °C.

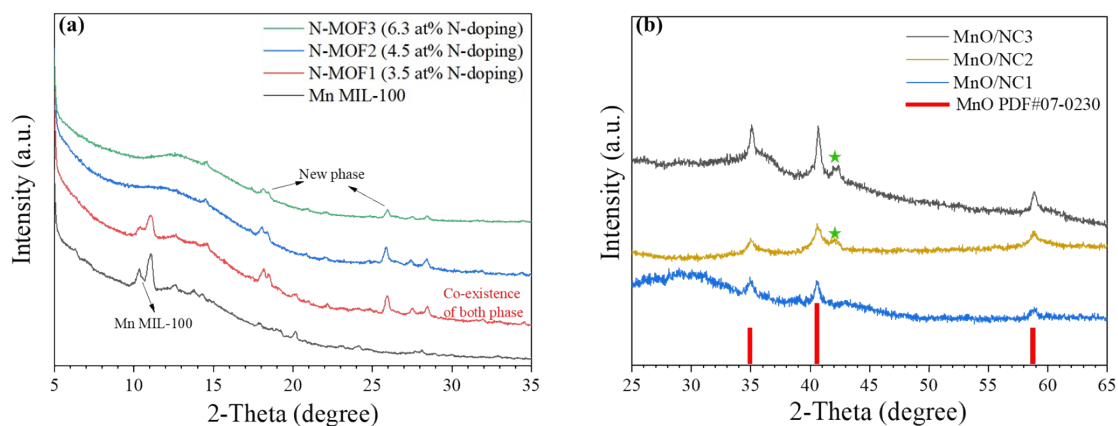


Figure S7. XRD results of (a) N-doped Mn MIL-100 at various doping level;
 (b) MnO/NC1-3 (The peak at the two-theta angle of 41.9 degree corresponds to $\text{Mn}_6\text{N}_{2.58}$).

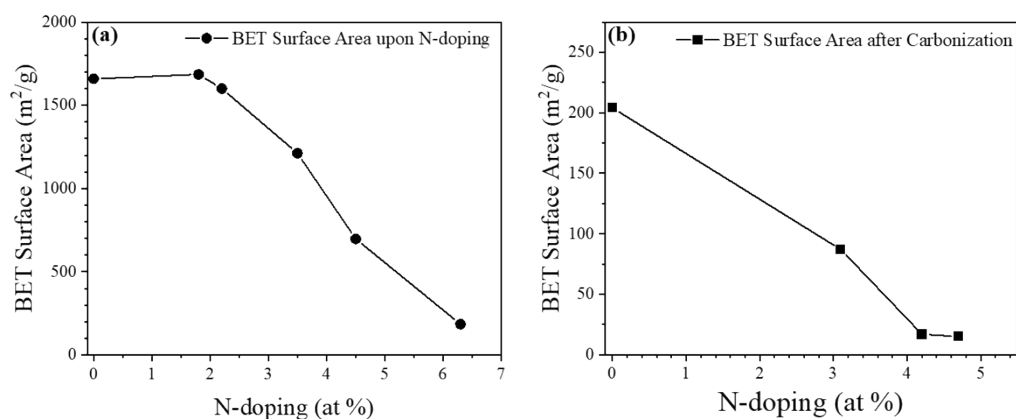


Figure S8. Plot of Brunauer–Emmett–Teller surface area calculated from N₂ adsorption of the N-doped samples and those samples after carbonization vs. the N content in the sample.

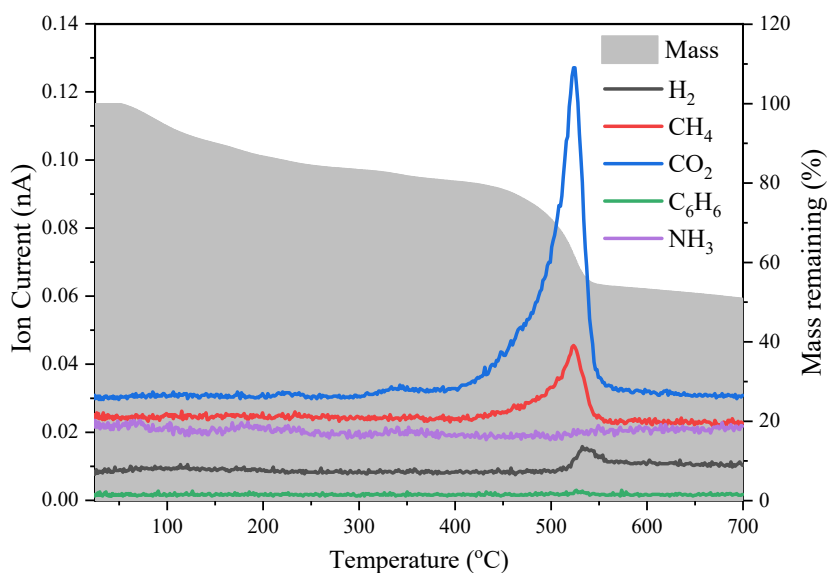


Figure S9. TG-MS result of the 3.5 at% N-doped Mn MIL-100 (Sample N-MOF1) conducted in N₂, ramping at 5 °C/min.

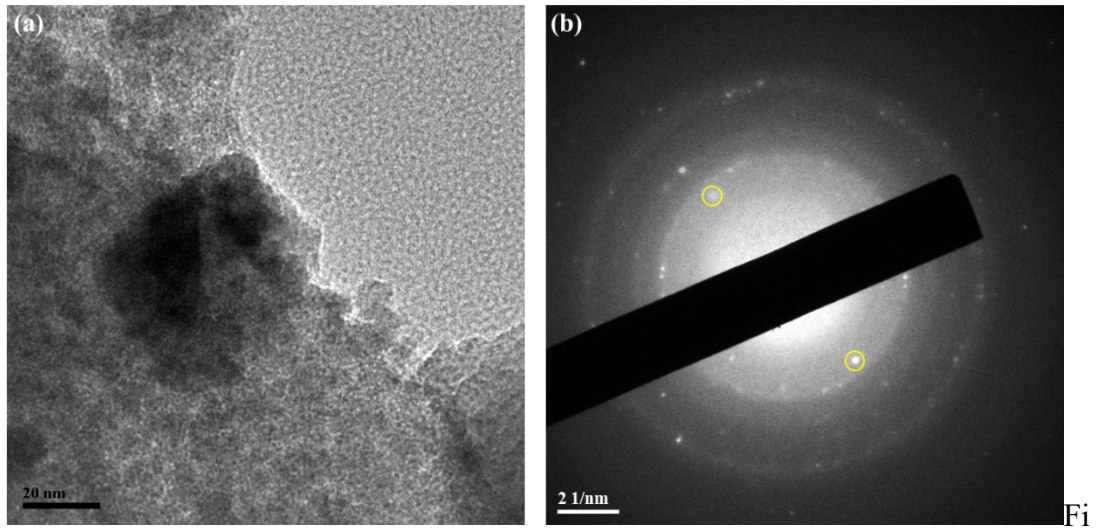


Figure S10. TEM and SAED of the 6.3 at% N-doped sample after carbonization (MnO/NC3-N700)

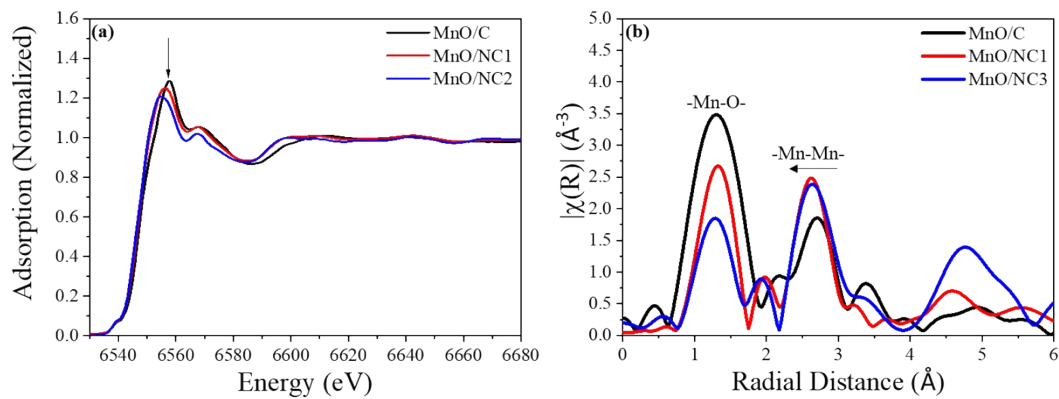


Figure S11. (a) Mn K-edge X-ray absorption near-edge structure (XANES) spectra and (b) Fourier transform of the extended X-ray absorption fine structure (EXAFS) spectra for MnO/C and different level of N-doped MnO/C.

Reference:

1. Reinsch, H. and N. Stock, *CrystEngComm*, 2013. **15**(3): p. 544-550.