

## Electronic Supplementary Information

### Modifying porous carbon nanofibers with $\text{MnO}_x\text{-CeO}_2\text{-Al}_2\text{O}_3$ mixed oxides for NO catalytic oxidation at room temperature

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#### 1.1 Preparation of $\text{MnO}_x\text{-CeO}_2\text{-Al}_2\text{O}_3$ mixed oxides

The process of prepare  $\text{MnO}_x\text{-CeO}_2\text{-Al}_2\text{O}_3$  mixed oxides refer to the X. Wu *et al.*' method<sup>1, 2</sup> completely.  $\text{MnO}_x\text{-CeO}_2$  mixed oxides with a molar ratio of 15:85 were synthesized by a citric acid-aided sol-gel method using  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (Yili, Beijing) and  $\text{C}_4\text{H}_6\text{MnO}_4 \cdot 4\text{H}_2\text{O}$  (Chemical Reagents, Beijing) as the precursors. The citric acid was added dropwise as the complexing agent with a 1.3:1 ratio of the acid to metal ions including  $\text{Ce}^{3+}$  and  $\text{Mn}^{2+}$ . Appropriate polyglycol was followed with the weight of 10% citric acid added. The blended solution was sufficiently mixed in a magnetic stirrer and heated at 80 °C till the transparent gel was formed. The resulting gel was dried at 110 °C overnight. The received powders were submitted to decomposition at 300 °C for 1 h and calcination at 500 °C for 3 h under static air in a muffle. The powders were cooled to room temperature (RT) in the furnace to obtain  $\text{MnO}_x\text{-CeO}_2$  mixed oxides.  $\text{MnO}_x\text{-CeO}_2\text{-Al}_2\text{O}_3$  mixed oxides were prepared by a similar method with the same Mn/Ce molar ratio and a weight ratio of  $(\text{Mn}_2\text{O}_3 + \text{CeO}_2):\text{Al}_2\text{O}_3 = 2:1$ . Cerium nitrate and manganese acetate were dissolved in deionized water and mixed with  $\gamma\text{-Al}_2\text{O}_3$  powders (BASF, 150 m<sup>2</sup>/g). Citric acid was added as the complexing agent with twice as the metal ions including  $\text{Ce}^{3+}$  and  $\text{Mn}^{2+}$ . Polyglycol was then added at 10% of the weight of citric acid. The solution was sufficiently stirred and heated at 80 °C until a porous gel was formed. The gel was dried at 110 °C overnight followed by decomposition at 300 °C for 1 h and calcination at 500 °C for 5 h under

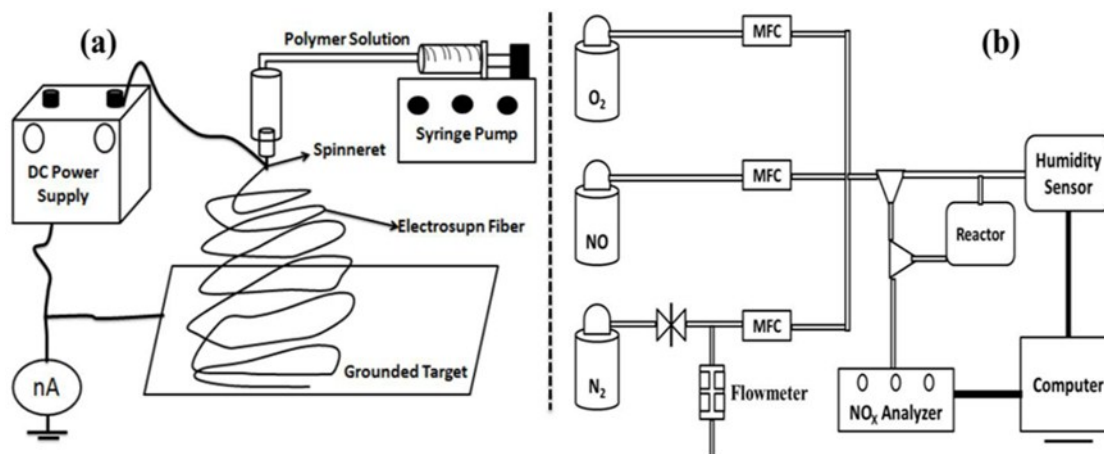
static air in a muffle<sup>1,2</sup>.

## 1.2 Preparation of PCNFs and MCAOs-PCNFs

The as-prepared  $\text{MnO}_x\text{-CeO}_2\text{-Al}_2\text{O}_3$  mixed oxides (5% weight ratio relative to PAN) were added into DMF, ultrasonically treated for 2 h, and then PAN was added and stirred vigorously at 333K for 24 h to obtain a homogeneous solution. Then the viscous polymer solution was electrospun as seen in the schematic diagram of the experimental set-up shown in Figure S1a. The dark color solution obtained was placed in a 20 mL syringe with a capillary tip (diameter is 0.5 mm). The anode of the high voltage power supply was clamped to a syringe needle tip; the cathode was connected to a metal collector. The electrospun fibers were collected on aluminum foil. The applied voltage was 25 kV, the distance between the tip and the collector was 19 cm, the flow rate of the spinning solution was 1 mL/h, and the relative humidity was approximately 20%. The as-spun nanofibers were stabilized by heating to 553K at a rate of 1°C/min in air, and maintaining them in this environment for 2 h. The stabilized fibers were carbonized for 10 min by heating to 1123K at a rate of 5°C/min in nitrogen and then the carbonized fibers were activated with  $\text{NH}_3$  for 10 min at 1123K. In fact, the  $\text{MnO}_x\text{-CeO}_2\text{-Al}_2\text{O}_3$  mixed oxides will be reduced partly at the reducing atmosphere.

The schematic diagram of the experimental setup to measure NO oxidation was displayed in Figure S1b. In the mixed gas section, three electronic mass flow controllers (MFCs) were used to control and measure the flow rates of  $\text{O}_2$ ,  $\text{N}_2$ , and NO. Gas mixtures were prepared from the pure gas streams by mixing in a stainless steel chamber. Gas mixtures could be fed to analytical instrumentation for calibration and measurement of inlet concentrations. A quartz tubular reactor ( $L = 100$  mm, i.d. = 5 mm) was filled with samples. The temperature was controlled via a water bath with a thermostat. A humidity sensor was used to measure the relative humidity. The  $\text{NO}_x$  analyzer (*42i model, Thermo electron Co., USA*) was used to detect the concentrations of NO and  $\text{NO}_2$ . The desired sample quantities (0.07 g) were packed in the tubular reactor and dipped in a water bath. The reactor was maintained at the desired reaction temperature to stabilize the system and provide a uniform bed temperature. The

required gas flow rates were adjusted using MFCs to obtain the desired concentrations of NO and O<sub>2</sub> in N<sub>2</sub>. The O<sub>2</sub> content was adjusted to 21 vol %. The inlet and outlet concentrations of the gases were measured by the NO<sub>x</sub> analyzer wherein the data obtained remains available for further analysis. In this study the inlet concentration was set at 50 ppm.



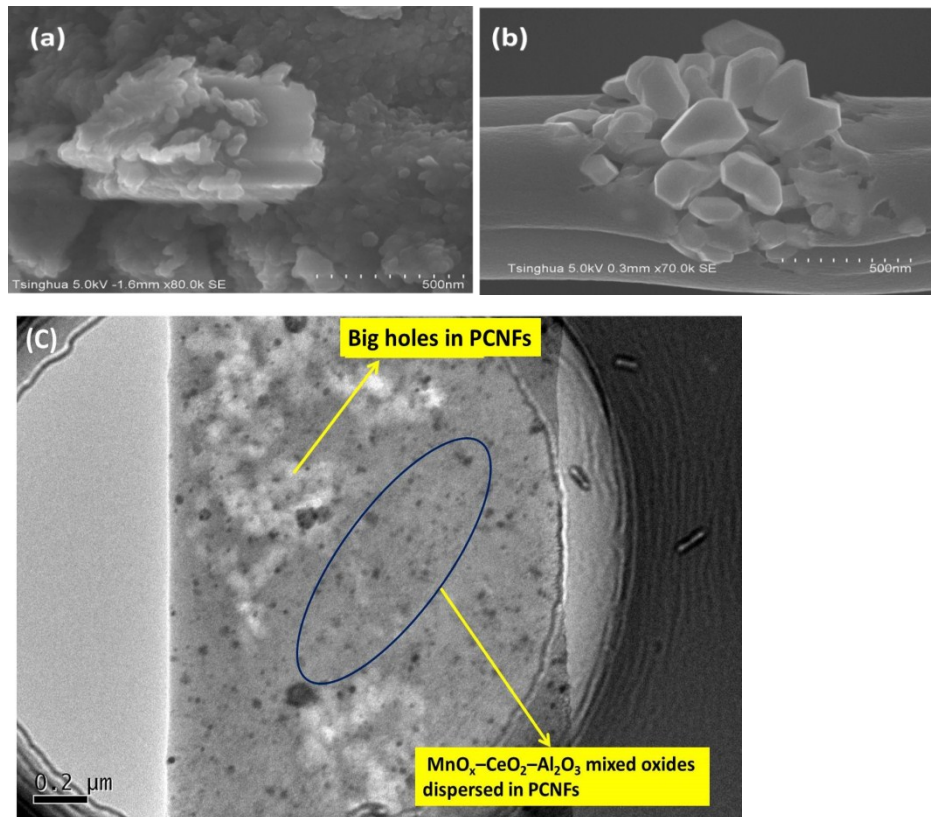
**Fig S1 Schematic of the experimental equipment (a) for electrospinning and (b) for testing NO catalytic oxidation**

### 1.3 Instrument for Characterization of PCNFs and MCAOs-PCNFs

The morphologies of the carbonized and activated PCNFs and MCAOs-PCNFs were examined by SEM in a LEO-1530. XRD (Rigaku D/Max 2500PC, Japan) were used to examine the structural properties of different samples. The specific surface areas and pore-size distributions of the samples were analyzed by physical adsorption of gases (N<sub>2</sub> at 77K) in volumetric adsorption systems (BELSORP-max, BEL, Japan). All samples were degassed at 195°C for 18h prior to the adsorption measurements. The total micropore volume (pores smaller than 2 nm) was calculated by applying the Horvath–Kawazoe (HK) equation. The specific surface areas of all samples were measured in a relative pressure interval of 0.05–0.30 by using the BET method. The micropore size distributions were calculated by applying the non-local density functional theory (NLDFT) to the N<sub>2</sub> isotherms using the Bel analysis software.

### 1.4 Micrograph of as prepared MnO<sub>x</sub>–CeO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> mixed oxides and MCAOs-PCNFs

Figure S2a shows the morphology of as prepared  $\text{MnO}_x\text{-CeO}_2\text{-Al}_2\text{O}_3$  mixed oxides. The diameters of nanoparticles are range from 50 to 100 nm and the  $\text{MnO}_x\text{-CeO}_2\text{-Al}_2\text{O}_3$  mixed oxides are apt to reunite with each other. Figure S2b displays the Scanning electron microscopy (SEM) image of  $\text{MnO}_x\text{-CeO}_2\text{-Al}_2\text{O}_3$  mixed oxides nanoparticles embed in PCNFs. The diameter of PCNFs about 500 to 600 nm which are far bigger than the diameter of  $\text{MnO}_x\text{-CeO}_2\text{-Al}_2\text{O}_3$  mixed oxides, thus, the nanoparticles can be encapsulated in PCNFs facilely. During the process of preparation of composite CNFs (MCAOs-PCNFs),  $\text{MnO}_x\text{-CeO}_2\text{-Al}_2\text{O}_3$  mixed oxides nanoparticles were added to the DMF with surface dispersant (lauryl sodium sulfate) forming suspension liquid, in which  $\text{MnO}_x\text{-CeO}_2\text{-Al}_2\text{O}_3$  nanoparticles were dispersed in DMF. And then PAN were added into the soliquid forming uniform solution for electrospinning, and after the heat treatment it also can maintain the uniformity, it was shown in figure S2c. During the carbonization, the  $\text{MnO}_x\text{-CeO}_2\text{-Al}_2\text{O}_3$  nanoparticles react with carbon and forming big holes in PCNFs.



**Figure S2 (a) the SEM image of as prepared  $\text{MnO}_x\text{-CeO}_2\text{-Al}_2\text{O}_3$  mixed oxides nanoparticles; (b) the nanoparticles embed in PCNFs and reunite with each other; (c)  $\text{MnO}_x\text{-CeO}_2\text{-Al}_2\text{O}_3$  mixed oxides nanoparticles disperse in PCNFs substrate uniformly.**

**Table S1. Pore structure and specific surface area parameters of the MCAOs-PCNFs and PCNFs**

Sample	S <sup>a</sup> (m <sup>2</sup> /g)	S <sub>m</sub> <sup>b</sup> (m <sup>2</sup> /g)	V <sub>T</sub> <sup>c</sup> (cm <sup>3</sup> /g)	V <sub>m</sub> <sup>d</sup> (cm <sup>3</sup> /g)
MCAOs-PCNFs	463	389	0.484	0.201
PCNFs	481	429	0.226	0.166

<sup>a</sup> S: specific surface area by the multi-point BET method ( $P/P_0$  from 0.004 to 0.04).

<sup>b</sup> S<sub>m</sub>: micropore surface area by the t-plot method.

<sup>c</sup> V<sub>T</sub>: total pore volume according to the capacity of the N<sub>2</sub> adsorption isotherm at  $P/P_0$  of 0.99.

<sup>d</sup> V<sub>m</sub>: micropore volume by the t-plot method.

## References

1. X. Wu, F. Lin, H. Xu and D. Weng, *Applied Catalysis B: Environmental*, 2010, **96**, 101-109.
2. X. Wu, S. Liu, D. Weng, F. Lin and R. Ran, *Journal of hazardous materials*, 2011, **187**, 283-290.