

## Supporting Information

# Effect of N-Doped Carbon on the Morphology and Oxygen Reduction Reaction (ORR) Activity of a Xerogel-Derived Mn(II)O Electrocatalyst

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The N-CC and MnO/N-CC catalysts were analyzed for their morphology using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The crystallographic characteristics of MnO nanoparticles and the graphitic properties of the carbon matrix are evaluated through X-ray diffraction analysis. The valence states of  $Mn^{n+}$  and the various chemical functionalities of the elements (C, N, O, and Mn) in the catalyst are evaluated using X-ray photoelectron spectroscopy (XPS). The N-CC and MnO/N-CC catalysts were evaluated for the oxygen reduction reaction (ORR) in nitrogen and oxygen-saturated 0.1 M KOH aqueous electrolyte, utilizing a conventional three-electrode system comprising a glassy carbon working electrode, a saturated calomel reference electrode, and a graphite rod counter electrode. Various electrochemical techniques, including cyclic voltammetry, linear sweep voltammetry, chronoamperometry, and rotating disk electrode measurements, were employed in the assessment. Comprehensive details regarding the experimental and ORR assessment methodologies are provided below.

### S1. Physical and electrochemical characterizations

Particle size, graphitic nature of the N-CC and MnO/N-CC catalysts are studied by using powder X-ray diffraction (XRD, Rigaku (D/Max-2500) diffractometer) analysis with Cu-K $\alpha$  radiation source ( $\lambda = 1.5406 \text{ \AA}$ ). The morphology of the MnO/N-CC catalysts are studied by scanning electron FESEM (Hitachi SU8220) and transmission electron microscope (FETEM, Titan G2 ChemiSTEM Cs Probe (FEI Company, The Netherlands). The oxidation state of Ce and identification of different bonding of N and C are examined by X-ray photoelectron spectroscopy (XPS) using a Thermo Scientific K-Alpha X-ray photoelectron spectrometer.

### S2. Electrochemical Characterizations of the N-CC and MnO/N-CC catalysts

Electrochemical studies of the MnO/N-CC catalysts are studied in a traditional three electrode system with glassy carbon electrode (effective surface area of  $0.1257 \text{ cm}^2$ ) as working electrode, graphite rod and saturated calomel electrode as counter and reference electrodes, respectively. The electrochemical studies were performed by using Biologic instruments SP-150e, potentiostat/galvanostat in 0.1 M KOH. For rotating disk studies, catalyst (MnO/N-CC and N-CC catalysts or Pt/C) ink is made by dispersing 4 mg of the catalyst in 1 mL of ethanol: water mixture (1:3) and the solution is ultrasonicated for 30 mins, to which a Nafion solution (5 wt.%) of 15  $\mu\text{l}$  is added and further ultrasonicated for 30 mins. A 14  $\mu\text{l}$  of the resultant catalyst ink is deposited in the glassy carbon electrode and then allowed it to dry at room temperature (catalyst loading:  $560 \mu\text{g cm}^{-2}$ ). For comparison, the Pt/C catalyst (10 wt%) with a catalyst loading of  $110 \mu\text{g cm}^{-2}$  is also deposited on the GCE.

The ORR electrochemical tests were performed by cyclic voltammetry (CV) and linear sweep voltammetry (LSV). Before the electrochemical tests, the electrolyte 0.1 M KOH solution is saturated with  $N_2/O_2$  gas. The CV and LSV curves were recorded in the potential range of 0-1.2 V vs. RHE with a scan rate of 50 and 10  $\text{mV s}^{-1}$ , respectively. For Koutechy-Levich (K-L) plots, the LSV curves were recorded at different rotations speeds from 800 to 2400 rpm. The number of electrons transferred in ORR process at different electrode potentials are calculated

from the slopes of Koutechy-Levich (K-L) plots i.e plots of  $j^{-1}$  vs.  $\omega^{-1/2}$  using the following questions.

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{j_L} \quad (s1)$$

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{B\omega^{1/2}} \quad (s2)$$

$$B = 0.62 n F C_{O_2} D_{O_2}^{2/3} \nu^{-1/6} \quad (s3)$$

where  $j$  is measured current density,  $j_L$  is diffusion-limiting current density,  $j_k$  is kinetic current density,  $\omega$  is angular velocity ( $\text{rad s}^{-1}$ ).  $B$  is a parameter calculated from the equation (3); “ $n$ ” is number of electrons transfer per  $O_2$  molecule, where  $j$  is measured current density,  $j_k$  is kinetic current density,  $j_L$  is diffusion limited current density,  $\omega$  is electrode rotation rate,  $F$  is Faraday constant ( $96,485 \text{ C mol}^{-1}$ ),  $C_0$  is bulk concentration of  $O_2$  ( $1.2 \times 10^{-3} \text{ mol L}^{-1}$  for both 0.1 M KOH solution and 0.1 M  $HClO_4$  solution),  $D_0$  is diffusion coefficient of  $O_2$  ( $1.9 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$  for 0.1 M KOH solution and  $1.93 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$  for 0.1 M  $HClO_4$  solution) and  $\nu$  is kinetic viscosity of the electrolyte ( $0.01 \text{ cm}^2 \text{ s}^{-1}$  for both 0.1 M KOH solution and 0.1 M  $HClO_4$  solution)

Tafel slope was calculated according to Tafel equation:

$$E = a + b \log(j)$$

Where  $E$  is the applied potential in the LSV test,  $a$  is a constant,  $b$  is the Tafel slop and  $j$  is the current density.

The stability of the MnO/N-CC-5 and Pt/C catalysts have been carried out by potential cycling of the working electrode by recording repeated cyclic voltammograms between 0 to 1.23 V vs. RHE for 5000 at the scan rate of  $50 \text{ mV s}^{-1}$ . To assess the degradation of the catalysts, the LSVs were recorded after stability test in  $O_2$  saturated 0.1 M KOH electrolyte with a scan rate of  $10 \text{ mV sec}^{-1}$ . All the potential was represented on relative hydrogen electrode (RHE) scale for convenience. Chronoamperometric (CA) measurements were also used to judge the stability of the catalysts with the potential holding at 0.7 V (vs. RHE) in  $O_2$ -saturated 0.1 M KOH electrolyte at a rotating rate of 500 rpm.

For electrochemical surface area measurements: For various MnO/N-CC catalysts, normalizing the double layer capacitance CDL with the specific capacitance  $C_s$  is used to get the ECSA according to equation

$$ECSA = C_{DL}/C_s$$

Non-Faradaic region is first identified by performing CV in  $N_2$  saturated 0.1 M KOH and the MnO/N-CC loaded GCE is cycled at different scan rates in this region. The plot of scan rate vs. current has a linear relation for both anodic and cathodic scans according to equation

$$i_c = vC_{DL}$$

$i_c$  is the capacitive current,  $v$  is the scan rate and  $C_{DL}$  is the double layer capacitance. The slope of this plot is obtained, and average of this slope is the double layer capacitance ' $C_{DL}$ '. ECSA is estimated by dividing double layer capacitance ' $C_{DL}$ ' with the specific capacitance ' $C_s$ '. Specific capacitance of  $40 \mu\text{F cm}^{-2}$  are used to calculate ECSA. The electrochemical surface area (ECSA) of Pt/C catalyst is determined by the method of hydrogen adsorption and desorption in  $\text{N}_2$ -saturated  $0.1 \text{ M KOH}$  solution at a scan rate of  $50 \text{ mV s}^{-1}$ .

Further, the ECSA are converted into  $\text{m}^2/\text{g}$  by using the mass of the catalyst loading is  $560 \mu\text{g cm}^{-2}$

**Formula:**

$$ECSA (\text{m}^2/\text{g}) = \frac{ECSA (\text{cm}^2)}{m_{\text{cat}} (\text{g})} \times 10^4$$

Where:

- $ECSA (\text{cm}^2)$  is the calculated ECSA from the previous step.
- $m_{\text{cat}} (\text{g})$  is the mass of the catalyst on the electrode.
- The factor  $10^4$  converts  $\text{cm}^2$  to  $\text{m}^2$ .

All the potential is shown on RHE scale, by the following equation.

$$E^{\circ}_{\text{RHE}} = E^{\circ}_{\text{SCE}} + 0.0059 * 13 (0.1 \text{ M KOH pH}) + 0.241 \text{ V (Standard potential of SCE)}$$

To obtain the tafel slopes, the LSV curves are mass transport corrected using the following equation

$$i_k = \frac{i \times i_d}{i_d - i}$$

$i_k$  is the mass-transport corrected kinetic current density,

$i_d$  is the measured diffusion limited current density, and

$i$  is the measured current density

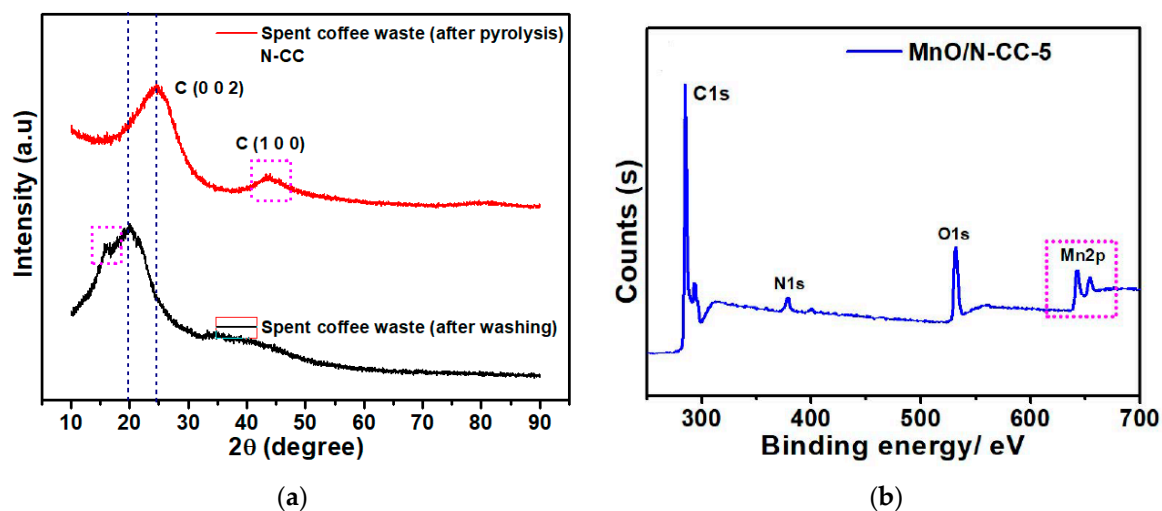


Figure. S1. (a) XRD patterns of washed spent coffee waste and after pyrolysis (b) XPS survey spectrum of MnO/N-CC-5 catalysts

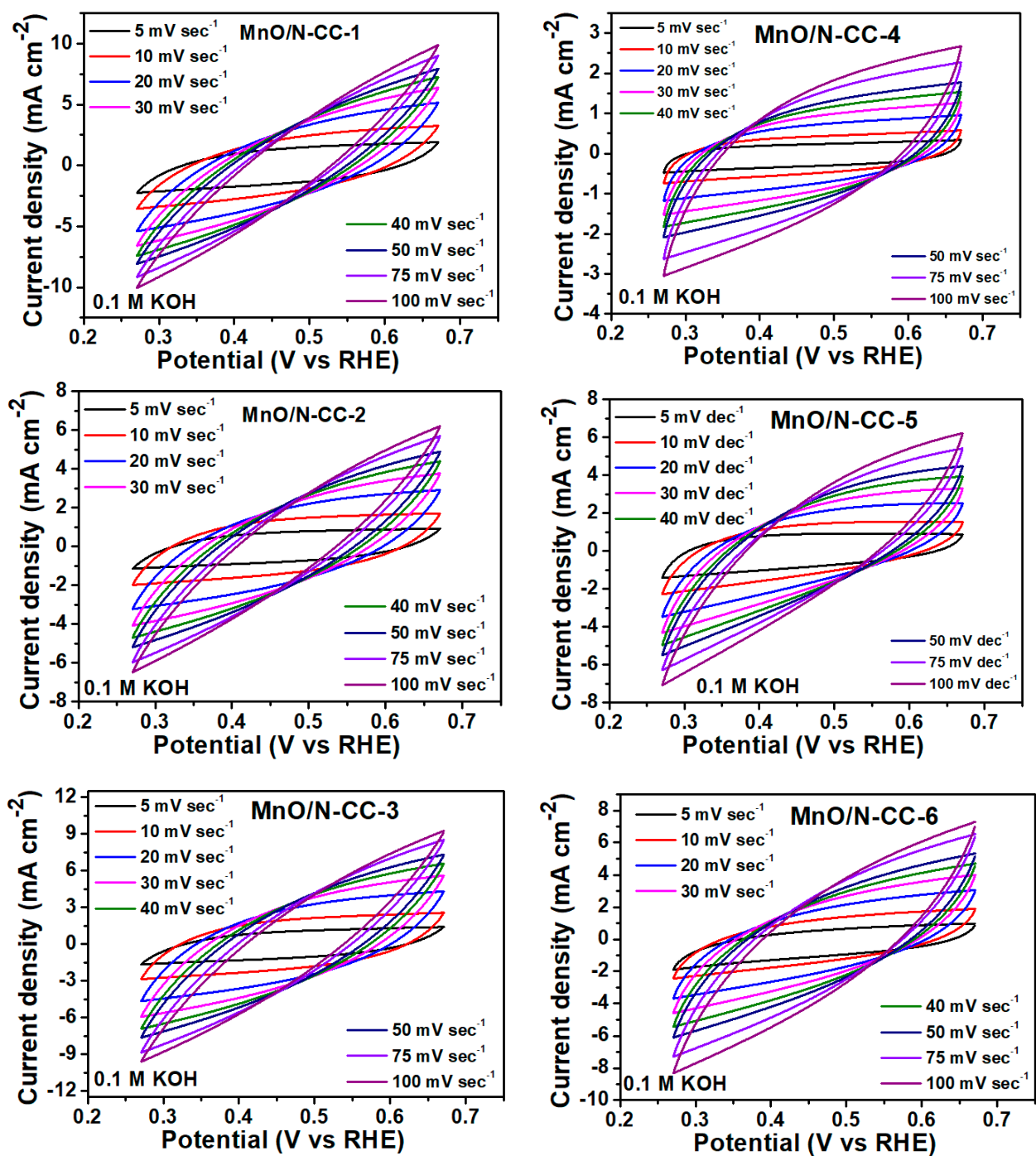


Figure. S2. Cyclic voltammograms of various MnO/N-CC catalysts in N<sub>2</sub> saturated 0.1 M KOH electrolyte with different scan rates.

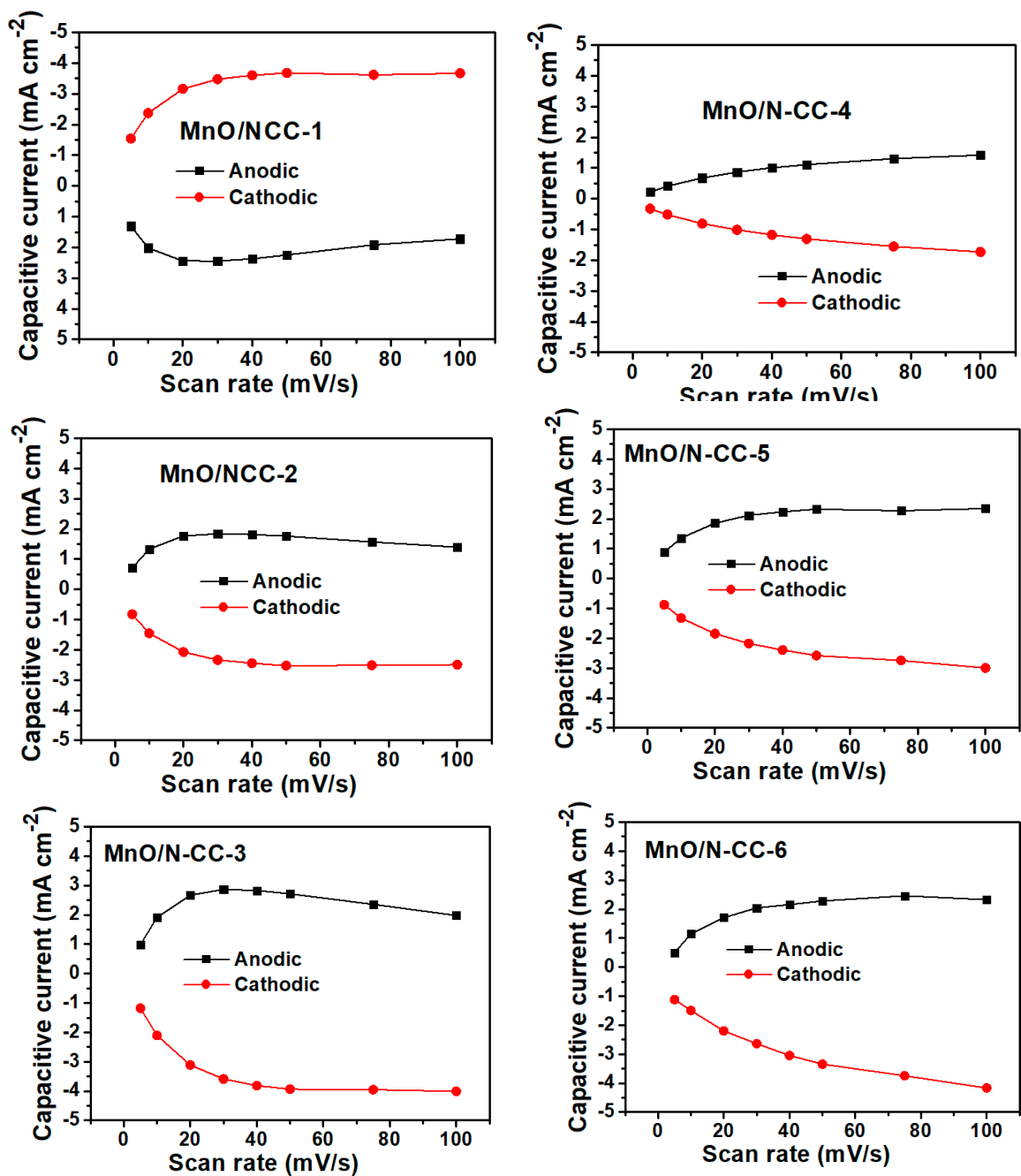


Figure. S3. Plots of capacitive currents vs scan rates of various MnO/N-CC derived from the cyclic voltammograms.

Table S1. Relationship between ECSA and half-wave potentials of various MnO/N-CC catalysts

Catalyst	Half-wave potential (V) vs RHE	ECSA (m <sup>2</sup> /g)
MnO/N-CC-1	0.62	0.56
MnO/N-CC-2	0.67	1.18
MnO/N-CC-3	0.69	2.40
MnO/N-CC-4	0.70	3.29
MnO/N-CC-5	0.78	4.07
MnO/N-CC-6	0.71	5.17
Pt/C (10 wt%)	0.81	-