Post modification of MOF derived carbon via g-C₃N₄ entrapment for efficient metal free oxygen reduction reaction

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Supporting Information

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Part S1: Detailed synthesis of MOFCN electrocatalysts

Materials and methods:

Melamine, potassium hydroxide (KOH), zinc nitrate hexahydrate, terephthalic acid and diethylformamide (DEF) were procured from M/s. Aldrich Chemicals. Isopropyl alcohol (IPA) and ethanol were obtained from Rankem Chemicals. All the chemicals were used as received without any further purification. A poly (tetrafluoroethylene) (PTFE) filter paper (pore size, 0.45 µm; Rankem) was used for the filtration. A copper grid with a carbon support (Icon Analytical Inc.) was used for the HRTEM observations.

1. Synthesis of MOF-5:

The synthesis of MOF-5 was carried out as per the standard procedure reported elsewhere¹. In brief, a mixture of zinc nitrate hexahydrate (0.4 g) and terephthalic acid (0.1 g) in 10ml diethylformamide (DEF) was sonicated for 10 min and heated at 90 °C for 3 days. The crystals obtained were later filtered and dried at 60 °C.

2. Synthesis of MOFCN catalysts:

In the first route, the MOF-5 crystals were transferred into an alumina boat and carbonized at 1000 °C at a heating rate of 5 °C/min in Ar atmosphere for 3 h. The final product was collected, washed in DI water and dried overnight at 60 °C. The obtained end carbon was observed to resemble the structure of the original MOF crystals thereby proving the template nature of the MOF. This carbon was further used for the incorporation of melamine, which was taken as the nitrogen source. The nanoporous carbon samples derived from MOF-5 and melamine were ground together in a mass ratio of 1:5 by using mortar and pestle to get a uniform mixture. The mixture was then dispersed in ethanol followed by sonication for 30 min in a bath type sonicator followed by stirring for 12 h at room temperature in order to get a homogeneous mixture. The resulting material was then subjected to solvent evaporation by simultaneous heating and stirring at 60 °C till a solid material was obtained. The solid material was again heated in a flow of Ar atmosphere at 550 °C at a rate of 5 °C/min for 3 h followed by natural cooling to RT. This final product, denoted as MOFCN550, was used for the future studies. In the next step, the as synthesized MOFCN550 composite was further subjected to pyrolysis at 800, 900 and 1000 °C each and the samples were denoted as MOFCN800, MOFCN900 and MOFCN1000 respectively.

In the second route, as regularly followed in literature, direct impregnation of N source into the MOF crystal matrix was carried out wherein MOF-5 crystals and melamine precursors were dispersed in

ethanol and stirred overnight. The resulting solid was pyrolysed at 900 °C in an Ar flow and the resulting sample is denoted as MOF5-CN.

Part S2: Characterization of the prepared catalysts

The powder X-ray diffraction (PXRD) analyses of the catalysts were done using PANalytical X'pert Pro instrument, with the scan rate of 0.5° per min, with the 20 value ranging from 0 to 60,° using Cu Kα (1.5418 Å) radiation. The structure and morphology analysis were carried out using a high resolution transmission electron microscope (HR-TEM) FEI model TECNAI G² F30 instrument operated at an accelerating voltage of 300 kV (Cs = 0.6 mm, resolution 1.47 Å). TEM samples were prepared by dispersing the prepared catalysts in isopropyl alcohol followed by drop casting the suspension onto a 200 mesh copper grid coated with carbon film (ICON Analytical) and drying under lamp overnight. Elemental analysis were done using a scanning electron microscope (SEM) system (FEI, Model Quanta 200 3D) equipped with EDX (Energy dispersive X-ray) analysis attachment at an operating potential of 30 kV. Xray photoelectron spectroscopy (XPS) was done on a VG Microtech Multilab ESCA 3000 spectrometer that was equipped with an Mg K α X-ray source (hv = 1253.6 eV). Raman analysis of MOFC, MOFCN800, MOFCN900 and MOFCN1000 were performed on an HR 800 Raman spectrometer (Jobin Yvon, Horiba, France) using 632.8 nm green laser (NRS 1500 W) in order to obtain the graphitic, and defective nature of the carbon. Nitrogen adsorption-desorption experiments were conducted at 77 K using Quantachrome Quadrasorb automatic volumetric instrument using ultra pure N₂ (99.9995%). For the gas adsorption measurements, the samples were pre-activated at room temperature (for 24 h) and 100 °C (for 36 h) under ultrahigh vacuum (10-8 mbar) for overnight. About 50 mg of the samples were loaded for gas adsorption, and the weight of each sample was recorded before and after degassing in order to confirm the complete removal of all guest molecules in MOFC and MOFCN550. Thermogravimetric analyses were carried out by a Perkin Elmer STA 6000 analyzer from room temperature to 900 °C with a temperature ramp of 10 °C min ⁻¹.



Fig S1. PXRD patterns of MOF-5 and MOF5-CN.



Fig S2. TEM images of a) MOFC, b) MOFCN550 and c) MOFCN900.



Fig. S3. Raman analysis of the prepared samples MOFC, MOFCN800, MOFCN900 and MOFCN1000.



Fig. S4 XPS spectra, deconvoluted C 1s and N 1s spectra of MOFCN800 (a & b), MOFCN900 (c & d) and MOFCN1000 (e & f). The peak positions can be assigned, as C_1 , C_2 , C_3 , corresponds to C=C(sp²) at 284.5 eV, C-O at 285.83 eV , and C-N, at 287.9 eV respectively. Similarly for N 1s spectra the peak positions can be assighted N₁, N₂, N₃ corresponds to pyridinic N at 398.7 eV, pyrrolic N at 400.3 eV, and graphitic N at 401.4 eV respectively. Image (g) illustrates the presence of three types of N in the carbon matrix.

Table 1. Summary of the elemental composition of the prepared samples.

Sample Name	Element	Atomic Percentage (%)	Graphitic	Pyridinic	Pyrrolic
MOFCN800	С	73.1			
	Ν	8.26	41.68	36.12	21.88
	0	18.0			
MOFCN900	С	83.09			
	Ν	7.0	47.53	27.97	24.48
	0	9.45			
MOFCN1000	С	80.73			
	Ν	4.74	25.6	12.46	62.1
	0	14.52			



Fig. S5. Energy dispersive X-ray (EDX) analysis of MOFC, MOFCN900 and MOF5- CN

Figure S5 shows the EDX spectra and the elemental composition of the MOFC (Fig. S5a). The peak profile clearly shows the presence of C, O elements, without any traces of metal impurities. On nitrogen doping, i.e., in case of MOFCN900 (Fig S5b), the profile shows the addition of N element to the carbon matrix. It is important to note that the N content of 7.18 % observed through EDX analysis is in good agreement with the XPS results.



Quantification results

Element	Weight %	Atomic %	Uncert. %	Detector	k-Factor
				Correction	
C(K)	71.52	86.52	0.17	0.26	4.032
N(K)	1.11	1.15	0.02	0.26	3.903
O(K)	9.09	8.25	0.04	0.49	2.008
Zn(K)	18.27	4.06	0.05	0.99	1.686

Fig. S6. Energy dispersive X-ray (EDX) analysis MOF5- CN, obtained from direct method.



Fig. S7. TG analysis of the MOFCN550, obtained by heating from RT to 900 °C, in N_2 atmosphere.

The thermo gravimetric analysis of the MOFCN550 was performed by heating the sample from RT to 900 °C in N_2 atmosphere. The initial weight loss is mainly due to the solvent molecules. This is followed by a major weight loss region from 600 to 900 °C which can be attributed to the decomposition of g-C₃N₄ which begins at around 550 °C. Around 80 % weight loss suggests the completion of decomposition of g-C₃N₄, leaving behind residual carbon.

Part S3: Electrochemical studies of the prepared catalysts

All electrochemical experiments were done by using an Autolab PGSTAT 30 (Ecochemie) with conventional three-electrode system received from Pine Instruments. Hg/HgO (in 0.1 M KOH) and Pt wire were used as reference and counter electrodes respectively. The working electrode used was a glassy carbon (GC) electrode (5 mm diameter) embedded in Teflon. This electrode was polished on a polishing cloth using 0.3 μ m alumina slurry followed by washing with water and acetone. The sample coating on the working electrode was carried out as follows: 5 mg of catalyst was dispersed in 1 ml of ethanol in water (3:2) solution by sonication. 10 μ l aliquot of the prepared slurry was drop-casted on the GC electrode with the help of a micro syringe. Subsequently, 3 μ l of 0.1 % Nafion® solution in ethanol was coated on the surface as a binder. This electrode was further dried in air for 3 h and was used as the working electrode. 0.1 M KOH was used as the electrolyte for all the electrochemical studies. RRDE experiments were carried out at a scan rate of 10 mV/s. O₂ and N₂ were used to achieve oxygen saturated and oxygen-free environments respectively for the RDE experiments.

The number of electrons transferred per oxygen molecule in the ORR process is determined using Koutecky–Levich (K-L) equation and measuring the yield of H_2O_2 formation using RRDE analysis. The K-L equation relates the inverse of the current density (j⁻¹) and the inverse of the square root of the rotation speed ($\omega^{-1/2}$), and can be represented as follows,

$$\frac{1}{j_{\lim}} = \frac{1}{j_k} + \frac{1}{B \omega^{0.5}}$$

B=0.62nFC₀ (D₀)^{2/3} v^{-1/6} C₀₂

where, j_k is the kinetic current density, ω is the angular velocity and B is related to the diffusion limiting current density, also expressed in the above equation. Where, F is the Faraday constant (F= 96485 C mol⁻¹), C_{O2} is the bulk concentration of O₂ (1.2x 10⁻³ mol l⁻¹), v is the kinematic viscosity of the electrolyte (v=0.1 m² s⁻¹), and D is the diffusion coefficient of O₂ in 0.1 M KOH (1.9x10⁻⁵ cm² s⁻¹). K-L plots, which deals with the limiting current density (j) and square root of rotation speed ($\omega^{1/2}$), are presented in Fig3b.(It shows a linear relation between the current density and square root of the rotation speed in the potential range of -0.25 to -0.6 V.

The yield of H₂O₂ formed during RRDE analysis was calculated from the following formula,

% of H₂O₂₌
$$\left\{ (200 * \frac{I_r}{N}) / (I_d + \frac{I_r}{N}) \right\}$$

where $I_r = ring$ current, $I_d = disc$ current, and N = collection efficiency.



Fig. S8. Cyclic voltammograms of the prepared electrocatalysts in 0.1 M KOH electrolyte, with a scan rate of 10 mV/s, Pt wire as counter electrode and Hg/HgO as reference electrode were during the analysis.



Fig S9. Comparing the activity of the prepared catalysts with commercial Vulcan carbon, from linear sweep voltammograms analysis.

S.No	Sample	Onset potential (V vs. Hg/HgO)	Current density (mA/cm ²)	
1	Vulcan® XC72	-0.25	1.2	
2	MOF C	-0.1	3.0	
3	MOF5-CN	-0.095	2.70	
4	MOFCN800	0.0	3.74	
5	MOFCN900	0.035	4.20	
6	MOFCN1000	-0.02	3.40	
7	40 Pt C	0.1	5.60	

Table 2. Comparison of the onset potential and current density obtained from CV and RDE studies for all the prepared samples



Fig S10. RRDE analysis of the prepared catalysts, and measuring the H_2O_2 formation.

Table 3. Summary of the yield of H_2O_2 formed during RRDE analysis and electron transfer number calculated from K-L plots, of electrocatalysts under study:

Sample	H ₂ O ₂ yield (%)	No. of e ⁻ transferred
MOFC	56	2.20
MOFCN800	22	3.06
MOFCN900	12	3.12
MOFCN1000	28	3.09



Fig S11. Linear sweep voltammograms of (a) PtC40 and (b) MOFCN900 before and after ADT in 0.1 M oxygen saturated KOH at a rotation speed of 1600 rpm and a scan rate of 10 mV/ S. Pt wire as the counter electrode and Hg/HgO as the reference electrode were used in the study.

References	Precursor	Medium	Over potential difference	Currrent density (mA/cm²)	Reference electrode
2	CMK3+ Cyanamide	0.1 M KOH	100 mV	3.5	Ag/AgCl
3	GO + Co + THPP	0.1 M KOH	120 mV	4.0	Ag/AgCl
4	GO + ethylene diamine + Silica	0.1 M KOH	100 mV	7.3	Ag/AgCl
5	Glucose + Cysteine	0.1 M KOH	>100 mV	-	Ag/AgCl
6	Graphene + NH ₃	0.1 M KOH	200 mV	0.8 (7.5 ug loading)	Ag/AgCl
7	Glucose + SiO2 Cyanamide	0.1 M KOH	>80 mV	5.0	Ag/AgCl
Present study	MOF derived carbon + melamine	0.1 M KOH	65 mV	4.2	Hg/HgO

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