Electronic Supplementary Information (ESI)

Elucidating the oxygen reduction reaction kinetics on defect engineered nanocarbon electrocatalyst: Interplay between N-dopant and defect sites

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Experimental details

Synthesis method

DG was prepared using melamine (as a carbon and nitrogen precursor) and zinc powder (as a template) taken in 1:1 ratio. The two were mixed completely using mortar pastel and then annealed at 800 °C under argon atmosphere for 2 h with ramp rate of 3 °C min⁻¹ to form carbon framework. Thereafter, the as prepared carbon material was annealed at different temperatures: 950 °C, 1050 °C, 1150 °C at a rate of 3 °C min⁻¹ under flowing argon gas and maintained at this temperature for 2 h to form defects by evaporation of Zn and nitrogen from the carbonized material and were named as DG-T. (T= 950, 1050, 1150 °C). The ratio of melamine and zinc were also varied as 1:2, 1:1, 2:1 and 10:1 to check the effect of amount of Zn in the product and the same annealing procedure was followed, first carbonization at 800 °C and then removal of Zn, N at 1050 °C (optimized for ORR). Also, to determine the effect of nitrogen, only carbon source i.e., dextrose and Zn were used to prepare C_{1:1} at 800 °C followed by 1050 °C.

Instrumentation.

X-ray diffraction (XRD) patterns of the samples to investigate the crystal structure were obtained from an X-ray diffractometer (Bruker D8 Advances instrument) with Cu-K α (λ = 1.5406 Å) radiation in the 20 range from 10° to 70° with an acceleration voltage of 40 KV.

The detailed surface microstructure of samples was analyzed by a transmission electron microscope (TEM, JEM2100 instrument).

Bruker Multimode 8 atomic force microscope (AFM) was utilized to examine the topography and thickness of the nanosheets deposited on freshly cleaved micas.

For surface area analysis, N2 adsorption/desorption tests were carried out at 77 K by a gas adsorption analyzer (Autosorb IQ Quantachrome instrument). The Brunauere-Emmette-Teller (BET) and Barrett-Joyner-Halenda (BJH) models were used to calculate the specific surface area and pore size, respectively of the samples, respectively.

The defective nature of the samples was shown by Raman spectra obtained from WITEC Focus Innovations Alpha-300 Raman confocal microscope under an excitation laser of 532 nm.

The surface elemental composition and bonding configuration of the prepared samples was determined using X-ray photoelectron spectroscopy (XPS) spectrometer (K-Alpha 1063) instruments in an ultrahigh vacuum chamber ($7X10^{-9}$ torr) using Al-K_a radiation (1486.6 eV).

The NEXFAS spectra were measured in Beamline at Indus-2 (DMP/MG), UGC-DAE CSR, Indore under an ultra-high vacuum (UHV) chamber maintained at base pressure of 5x10⁻¹⁰ mbar. The measurements were taken in the Total electron yield (TEY) mode.

Electrochemical Characterizations

Electrochemical characterizations were performed in a three-electrode cell using a Metrohm multichannel Autolab (M204) electrochemical workstation at room temperature. A catalyst coated rotating ring-disk electrode (RRDE; GC disk area 0.196 cm²; Pt ring area 0.041 cm²) was used as working electrode, Ag/AgCI (3 M KCI) as reference electrode and Pt wire as counter electrode.

Formula used for the calculations:

All the potentials were calibrated vs RHE by using the equation:

$$E_{RHE} = E_{Ag/AgCl} + 0.0591 \, pH + 0.210 \tag{1}$$

All the electrochemical measurements (cyclic voltammetry (CV) and linear sweep voltammetry (LSV), chronoamperometry) were carried out in 0.1 M KOH (pH >13) solution that was saturated with O_2 for

30 min prior to the reaction and also during the reaction O2 saturation was maintained. As the system achieved equilibrium, the data was recorded at the scan rate of 10 mV s-1. During linear sweep voltammetry test, the rotation speed of the working electrode was increased from 625 to 4900 rpm at the scan rate of 10 mV s-1. The diffusion-limiting $({}^{j}L)$, kinetic current densities $({}^{j}K)$ and the number of electrons transferred (n) per O₂ molecule were calculated from the slopes (B) of the best linear fit lines of KL plot using KL equation which is given by:

$$\frac{1}{j} = \frac{1}{j_L} + \frac{1}{j_K} = \frac{1}{\frac{1}{Bw^2}} + \frac{1}{j_K}$$

$$Bw^{\frac{1}{2}} ; \qquad (2)$$

Where *j* is the measured current density, diffusion-limiting $({}^{j_L})$, kinetic current densities $({}^{j_K})$ and the number of electrons transferred (n) per O2 molecule, *w* is rotating speed in rpm and B is the Levich slope.

B is given by:

$$B = 0.62 \ nFC_0 D_0^{3/2} \vartheta^{-1/6}$$
(3)

where F is the Faraday constant (F = 96485 C mol⁻¹), C_0 is the bulk concentration of O₂ in the solution, D_0 is the diffusion coefficient of O₂ in 0.1 M KOH (1.93 × 10⁻⁵ cm² s⁻¹), ϑ is the kinematic viscosity of the electrolyte (1.09× 10⁻² cm² s⁻¹).

The number of electrons transferred (n) and H_2O_2 production yield is calculated from the RRDE measurement using equations:

$$n = 4 \times \frac{I_D}{\frac{I_R}{N} + I_D}$$

$$H_2O_2(\%) = 200 \times \frac{\frac{I_R}{N}}{\frac{I_R}{N} + I_D}$$
(4) and (5)

where *n* is the number of electrons transferred (n) during the ORR process, I_D and I_R is the absolute value of the disk and ring current resp. and *N* is the current collection efficiency of the Pt ring (0.249 in this work).

Electrode preparation

The catalyst ink was prepared by dispersing 1 mg of the DG-T in 300 uL of water by ultrasonication for an hour to form a homogenous ink. Prior to dropcasting, the RRDE electrode was cleaned thoroughly by polishing it with 1, 0.3, and 0.05 µm alumina powder and was washed ultrasonically in deionized (DI) water. The optimized mass loading of the catalyst ink was coated on the surface of RRDE electrode and was then vacuum-dried. For comparison, a separate Pt/C solution was prepared by dispersing the Pt/C in a water and isopropyl alcohol mixture (1:1) containing Nafion (5 %) followed by ultrasonication for 30 min.

Theoretical study

Theoretical calculations are performed using density functional theory (DFT) as implemented in the PWscf package of the Quantum ESPRESSO distribution.[1,2] Generalized Gradient Approximation (GGA) with Perdew–Burke–Ernzerhof (PBE) functional is used to describe the exchange and correlation effect[3]. Projector-Augmented Wave (PAW) pseudopotentials are employed to treat the interactions between the ion cores and valence electrons[4]. Plane-wave cutoff energy of 450 eV is

used in the calculations. The k-point sampling of the Brillion zone is obtained using a 1×9×1 mesh for model structures. The energies and force are converged within a threshold limit of 0.001 meV/per atom and 0.01 eV/Å respectively. The Fermi level was slightly broadened using a Marzari–Vanderbilt smearing of 50 meV. The vacuum of 15Å is considered to avoid the self-interaction between images.

Computational details:

Section S1:

Machine learning algorithm:

a. Calculations of simple linear fit predictive equation for $\Delta G_{\text{OH}}.[5]$

The linear fit of ΔG_{OH} values with $D_{\pi}(E_F)$ and R-O_{π} (Figure S12) gives a following relations,

$\Delta G_{OH} = -2.1 * D_{\pi}(E_{F}) + 0.99$	(6)
$\Delta G_{OH} = -14.99 * R - O_{\pi} + 0.99$	(7)

In eqn. (1) and (2), the intercepts are same (0.99). So, we can define a common function $F(\pi)$ as

follow,

$$F(\pi) = 7.14 * R \cdot O_{\pi} + D_{\pi}(E_F)$$
(8)

whereas, the value 7.14 is a slope of (2)/ (1) [14.99/2.1]. This function, $F(\pi)$ is varying linearly with ΔG_{OH} and gives a linear fit equation as follows, $\Delta G_{OH} = -1.16 * F(\pi) + 0.99$ (9)

b. Support Vector Regression (SVR):

Support Vector Regression is a supervised learning algorithm that finds the best fit line for the nonlinear dataset. In simple regression our goal is to minimize the error rate. But in SVR we try to fit the error within a certain threshold and the best fit line is the hyperplane that has the maximum number of points. The kernel functions transform the input data into a higher dimensional feature space to make it possible to perform the linear separation.[6,7]

$$f^{i}(x) = \theta_{0} + \sum_{j=1}^{i} \theta_{j} \phi_{j}^{i}(x)$$
(10)

where the parameters are obtained by minimizing the cost function,

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$$j(\theta) = \sum_{i=1}^{m} \nu(y^{i} - f^{i}(x)) + \frac{\lambda}{2} \sum_{j=1}^{n} \theta_{j}^{2}$$
(11)

One of the popular choice for the loss function, due to Huber (1964) is

$$\nu(x) = \begin{cases} \frac{r^2}{2}, & |r| \le c \\ c|r| - \frac{c^2}{2}, & |r| > c \end{cases}$$
(12)

where c is a predefined error constant. Using OLS one may obtain the form of the regression function,

$$f^{i}(x) = \left[\left(K(x^{i}, x^{i'}) + \lambda I \right)^{-1} y \right] K(x^{i}, x^{i'})$$
(13)

where, the parameters (θ_i) and the Kernel function (*K*) are represented by:

$$\theta = \frac{\phi(x)^T y}{K + \lambda I} \quad \text{and} \quad K(x^i, x^{i'}) = \langle \phi(x^i) \phi(x^{i'}) \rangle$$

c. Cross Validation

Cross-validation is a statistical method based on re-sampling technique, which helps to evaluate the performance of machine learning algorithms[8]. The k-fold cross validation is more popular that divides the given datapoints into k number of groups with different train/test datasets. Here, we used 5-fold cross validation with grid search hyperparameter tuning to find the accurate predictive performance of machine learning (ML) algorithms (MLR, RFR, SVR) with best hyperparameter settings. All 101 datapoints are used for training (80%) and testing (20%) the ML models in 5 different datasets alternatively.

d. Code for Support Vector Regression (SVR):

Importing Libraries

import pandas as pd

import numpy as np

import matplotlib.pyplot as plt

%matplotlib inline

Importing the dataset

import io

df = pd.read_csv(io.BytesIO(uploaded['ml.csv']))

Dataset is now stored in a Pandas Dataframe

df.head()

x = df.iloc[:, 0:2].values y = df.iloc[:, 2].values y = df.iloc[:,2].values y = y.reshape(-1,1)

Splitting the dataset into the Training and Test set from sklearn.model_selection import train_test_split

x_train, x_test, Y_train, y_test = train_test_split(x, y, test_size=0.2, random_state=4)

Feature Scaling

from sklearn.preprocessing import StandardScaler

sc_X = StandardScaler()

X_train = sc_X.fit_transform(x_train)

X_test = sc_X.transform(x_test)

sc_y = StandardScaler()

y_train = sc_y.fit_transform(Y_train)

Fitting SVR Regression to the dataset

from sklearn.svm import SVR

regressor = SVR(kernel = 'rbf')

regressor.fit(X_train, y_train)

y_pred = regressor.predict(X_test)

y_pred = y_pred.reshape(-1,1)

y_pred = sc_y.inverse_transform(y_pred)

y_pred

Predicting the Test set results

X_val = sc_X.transform([[0.1371, 0.0347846]])

y_val = regressor.predict(X_val)

y_val = y_val.reshape(-1,1)

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y_val = sc_y.inverse_transform(y_val)
```

y_val

Cross Validation

from sklearn.model_selection import import KFold, cross_val_score

crossvali = (cross_val_score(regressor, sc_X.fit_transform(x), sc_y.fit_transform(y), cv=5, n_jobs =1))

print(crossvali)

print(np.mean(crossvali))

e. Oxygen Reduction Reaction Pathways

Oxygen reduction reaction (ORR) can occur in both acidic as well as alkaline environment. In fourelectron pathway, the oxygen is reduced directly into two H_2O molecules in an acidic environment and generates four OH^- in an alkaline medium as follows [9],

$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	(acidic media)
$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$	(alkaline media)

But the ORR also can undergo through the two-electron pathway in which O_2 is reduced to H_2O_2 in an acidic medium and free OOH ions in an alkaline medium as the intermediate species as follows,

acidic media:

 O_2 + 2H⁺ + 2e⁻ \rightarrow H₂O₂

alkaline media:

 $O_2 + H_2O + 2e^- \rightarrow OOH^- + OH^-$

These intermediates hamper the efficiency of overall fuel cells. So, we need to find the selectivity of ORR pathways on a catalyst.

Therefore, we performed the DFT calculations to find the probability of formation of free OOH ion in the alkaline media for ideal site 21. (Free energy profile shown in **Figure S14**). We show that the step of free OOH ion formation is higher than formation of O* intermediate, which promoting the four electron ORR pathway on our ideal site 21. However, we also calculated the OHOH ion formation step (for acidic media), which shows a higher energy step as compared to step of O*. Therefore, we confirmed the four electron ORR is more favourable pathway over two electron pathways.

Section S2:

Calculation of adsorption free energies of molecules/intermediates for ORR and Free Energy Profile

In alkaline conditions, Oxygen Reduction Reaction (ORR) as,

 $O_2 + 2H_{2O}(l) + 4e^- \rightarrow 40H^-$

With the following reaction pathway,

 $O_2 + 2H_2 O(l) + 4e^- + *$

 $00H^* + H_{2\mathbf{O}}(l) + 0H^- + 3e^-$

 $0^* + H_2 \mathbf{O}(l) + 20H^- + 2e^-$

 $OH^{*} + 3OH^{-} +$

 $40H^{-} + *$

The free energy profile is an important tool to identify the reaction mechanism and thermodynamic overpotential of oxygen reduction reaction. The Gibbs free energies (G) are calculated by using the following equation, G = E+ZPE-TS-neU, where E is the DFT energy, ZPE is the zero-point energy, TS is the entropic term, n is the number of electrons transferred and U is the applied potential at the electrode [10]. Here, we have considered that the TS and ZPE of adsorbed atoms/ions are negligible to that of the gaseous phase at room temperature and ambient pressure. At equilibrium potential of U = 0.4 V in free energy profile, the first and last step are in the same energy level and the highest uphill step between any two adjacent energies is the potential determining step. The corresponding energy difference is known as thermodynamic overpotential. At onset potential, all the reaction steps becoming downhill with exothermic pathway.

Results and Discussions



Figure S1. (a) The various substitutional sites: S denotes the dopant site in red, filled circles and C represents the active sites in the graphene lattice. Doping represented by b) pyrrolic-N doping, c) oxidinic-N doping, and defects by d) 5-8-5 defect, e) 555-777 defect. The N, C, H represented by blue, wine, green colored spheres respectively.



Figure S2. Dependence of ΔG_{OH} on the (a) $D_{\pi}(E_F)$ and (b) R- $O_{\pi}[5]$



Figure S3. Scatter plots showing ΔG_{OH} predicted by various machine learning models on x-axis verses DFT computed ΔG_{OH} on y-axis.



Figure S4.TEM image of $DG_{1:1}$ -1050; inset: Selected area electron diffraction (SAED) pattern of $DG_{1:1}$ -1050.



Figure S5. Deconvoluted spectra of C 1s of DG_{1:1}-950, 1050,



Figure S6. Comparative CV plots of DG-10:1, 2:1, 1:1, 1:2 and C1:1 in 0.1 M KOH saturated with O_2 at 10 mV s⁻¹ scan rate.



Figure S7. Comparison bar plot of half-wave potential ($E_{1/2}$) and current density (*j*) of DG-10:1, 2:1, 1:1,1:2 and C-1:1.



Figure S8. Comparison bar plot of ORR onset potential (E_{onset}), peak potential (E_p (ORR)) and half-wave potential ($E_{1/2}$) of DG_{1:1}-950, 1050, 1150.



Figure S9. Comparative polarisation curves of DG-10:1, 2:1, 1:1,1:2 and C-1:1 in 0.1 M KOH saturated with O_2 at 1600 rpm.



Figure S10. UPS secondary cutoff (left) and valence (right) band region for $DG_{1:1}$ -950, 1050, 1150.



Figure S11. Ring and disk current of $\mathsf{DG}_{1:1}$ -1050 catalyst in O_2 saturated 0.1 M KOH at 1600 rpm.



Figure S12. Free energy profile of ORR with two and four electron pathway steps.



Figure S13. π orbital projected density of states of site 21 (a) before and after adsorption of (b) OOH, (c) O and (d) OH intermediate of ORR.



Figure S14. Lowdin charge analysis to understand the ORR intermediate adsorption.



Figure S15. The mechanism of ORR on active site 21 of $DG_{1:1}$ -1050.



Figure S16. STM image of $DG_{1:1}$ -1050 (a) at 20nm and (b) at 1 nm.

 $\textbf{Table S1:} The values of D_{\pi}(E_F), R-O_{\pi} \text{ and } \Delta G_{OH} \text{ (predicted using the SVR model) for model I.}$

Site	D _π (E _F)	R-O _π	ΔG _{OH} (SVR)
1	0.0282	-0.01217	0.93
2	0.0205	-0.02925	0.72
3	0.0231	-0.01274	0.93
4	0.00786	-0.01055	0.95
5	0.0296	-0.00088	0.98
6	0.014	-0.03336	0.65
7	0.0603	-0.02662	0.73
8	0.0215	0.037044	0.69
9	0.0298	0.052846	0.53
10	0.00292	0.011025	0.95
11	0.00867	0.016523	0.91
12	0.00646	-0.00177	0.99
13	0.046	0.036477	0.66
14	0.0379	0.020339	0.85
15	0.0173	0.026669	0.80
16	-0.00607	-0.00769	0.97
17	0.00216	0.008488	0.97
18	0.00264	-0.02206	0.83
19	0.0297	0.005447	0.97
20	0.0201	-0.02879	0.73
21	0.02186	-0.02419	0.79
22	0.0517	0.012388	0.91

 $\textbf{Table S2:} The values of D_{\pi}(E_F), R-O_{\pi} \text{ and } \Delta G_{OH} \text{ (predicted using the SVR model) for model II.}$

Site	D _π (E _F)	R-O _π	ΔG _{OH} (SVR)
1	0.0227	-0.03316	0.65
2	0.0442	-0.01866	0.85
3	0.00817	-0.01839	0.88
4	0.0464	0.001472	0.96
5	0.0884	-0.01609	0.82
6	0.0781	-0.00927	0.89
7	0.0109	-0.03156	0.69
8	-0.00664	0.024859	0.84
9	0.0526	-0.00161	0.95
10	0.179	0.016021	0.60
11	0.0885	0.0434	0.50
12	0.0291	0.005493	0.97
13	0.113	-0.01815	0.75
14	0.0199	0.037958	0.68
15	0.239	-0.0093	0.53
16	0.0535	0.042508	0.58
17	0.0397	0.065715	0.43
18	0.0928	-0.0245	0.71
19	0.0393	0.048512	0.55
20	0.0156	0.016846	0.90
21	0.143	0.04368	0.36
22	0.0434	0.031853	0.72
23	0.0324	0.007575	0.96
24	0.0242	0.012754	0.93
25	0.0331	-0.03379	0.64
26	0.02186	-0.03187	0.68
27	0.027	0.009211	0.95
28	0.093	0.029074	0.66
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Table S3: The values of $D_{\pi}(E_F),$ R-O_{\pi} and ΔG_{OH} (predicted using the SVR model) for model III.

Site	D _π (E _F)	R-O _π	ΔG _{OH} (SVR)
1	0.0149	-0.02363	0.81
2	0.0205	-0.02551	0.78
3	0.0128	-0.01829	0.88
4	0.0894	-0.00859	0.87
5	0.0284	-0.01531	0.90
6	0.0594	0.004301	0.94
7	0.027	-0.02825	0.73
8	0.0132	0.019746	0.88
9	0.031	-0.01326	0.92
10	0.057	0.029598	0.72
11	0.114	-0.00701	0.83
12	0.0417	-0.0038	0.96
13	0.101	-0.02815	0.64
14	0.0147	0.040131	0.66
15	0.132	-0.02658	0.61
16	0.0591	-0.00622	0.93
17	0.0674	0.009849	0.90
18	0.0954	-0.01102	0.85
19	0.0838	0.041644	0.53
20	0.00161	0.002272	0.99
21	0.195	0.002698	0.65
22	0.103	-0.00597	0.86
23	0.034	-0.00019	0.97
24	0.0249	0.015524	0.91
25	0.0371	-0.03478	0.62
26	0.066	-0.03021	0.66
27	0.0225	-0.01393	0.92
28	0.083	0.037417	0.58
29	0.0321	-0.01749	0.87

Table S4. Comparison table for different studies done on N-doped defective carbon catalysts.

Catalyst	Eonset	E _{1/2}	Stability	n	Specific surface area (m ² g ⁻¹)	Ref.
ND-GLC	0.991	0.875	8.3 h (84 %)	3.96	1348	[11]
NGM	0.89	0.77	8 h (98.5 %)	3.8	1100	[12]
NCN-1000-5	0.95	0.82	3.3 h (85.6 %)	3.92	1793	[13]
NLPC	0.92		5.5 h (96 %)	3.95	1579.3	[14]
DN-UGNR	0.957	0.808	8.3 h (84 %)	3.6	679	[15]
2D-PPCN	0.92	0.85	-	~3.6	1555.8	[16]
PD-C	0.91	0.83	10000 cycles (96 %)	~3.8	1147.6	[17]
NKCNPs-900	0.92	0.79	8h (78.8 %)	~4.0	841	[18]
DG _{1:1} -1050	0.96	0.82	12 h (98.01 %)	3.8	822	This work

ND-GLC: Pyridinic-N dominated and defect-enriched graphene-like carbon nanomaterial

NGM: Nitrogen-doped graphene mesh

NCN-1000-5: N doped ultrathin carbon nanosheets at 1000 1C with a mass ratio of 1:1

NLPC: 3D nanosheet-linked-polyhedron carbon

DN-UGNR: defect-rich N-doped ultranarrow graphene nanoribbons

2D-PPCN -2D phosphorus-doped porous carbon nanosheets

PD-C -defect-rich carbon nanomaterial

NKCNPs-900- N-doped carbon nanoparticles

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