Supporting Information

Electrochemical estimation of active site density on metal-free carbon-based catalyst

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Key words: active site density; adsorption; anthraquinone-2-sulfonate; ESA; nitrogen-doped carbon; oxygen reduction reaction; turnover frequency; wetted surface area

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Table S1 Charge of adsorbed-catechol on N/C 900 recorded after cycling in catechol solution of different concentrations.

Catechol concentration (mM)	Charge of adsorbed-catechol (mC)
1	0.91
5	3.10
50	6.46
100	6.78
200	6.80

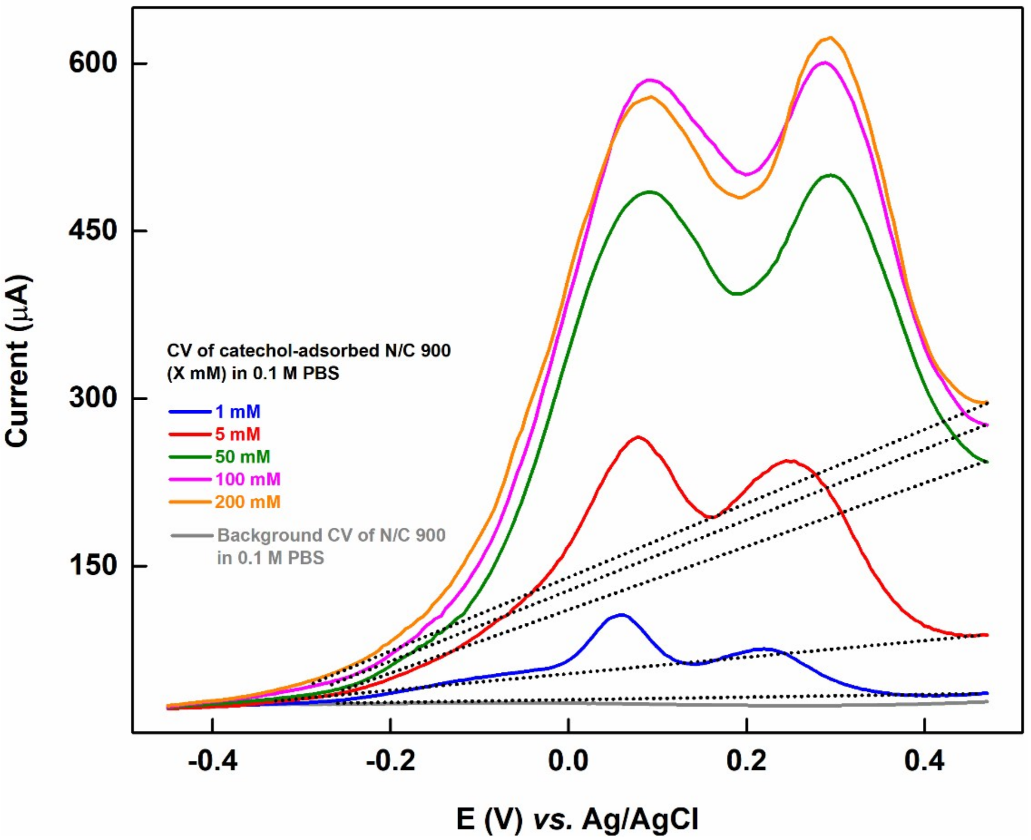

Figure S1 Voltammograms of the catechol-adsorbed N/C 900 catalyst recorded in argon-saturated 0.1 M PBS (pH 7) at 20 mV s^{-1} scan rate after cycling in different concentrations of catechol. Gray line represents the background voltammogarm of N/C 900 recorded in AQS-free argon-saturated 0.1 M PBS (pH 7) at 20 mV s^{-1} scan rate.

S1. Replacement of AQS with catechol and the polymerization of catechol

The problem related to the catechol-adsorption method is investigated by replacing the surface-adsorbed AQS with catechol molecule. **Figure S2** shows the voltammograms for the replacement of adsorbed-AQS on electrode surface by the oxidized products of catechol. N/C 900 is chosen as the representative catalyst surface. The red-colored wave represents the voltammogram of the AQS-adsorbed N/C 900 catalyst recorded in argon-saturated 0.1 M PBS (pH 7). The blue-colored voltammogram shows the gradual decrement in charge of adsorbed-AQS and the gradual increment in charge due to the adsorption of oxidized product of catechol during potential cycling in the presence of 20 mM catechol. It is observed that the adsorbed-AQS is removed from the surface completely after 20 cycles; no oxidation peak is observed in the forward cycle of the voltammogram due to adsorbed-AQS. The pink-colored wave represents the voltammogram of catechol-adsorbed N/C 900 after removing the adsorbed-AQS molecule from the surface completely.

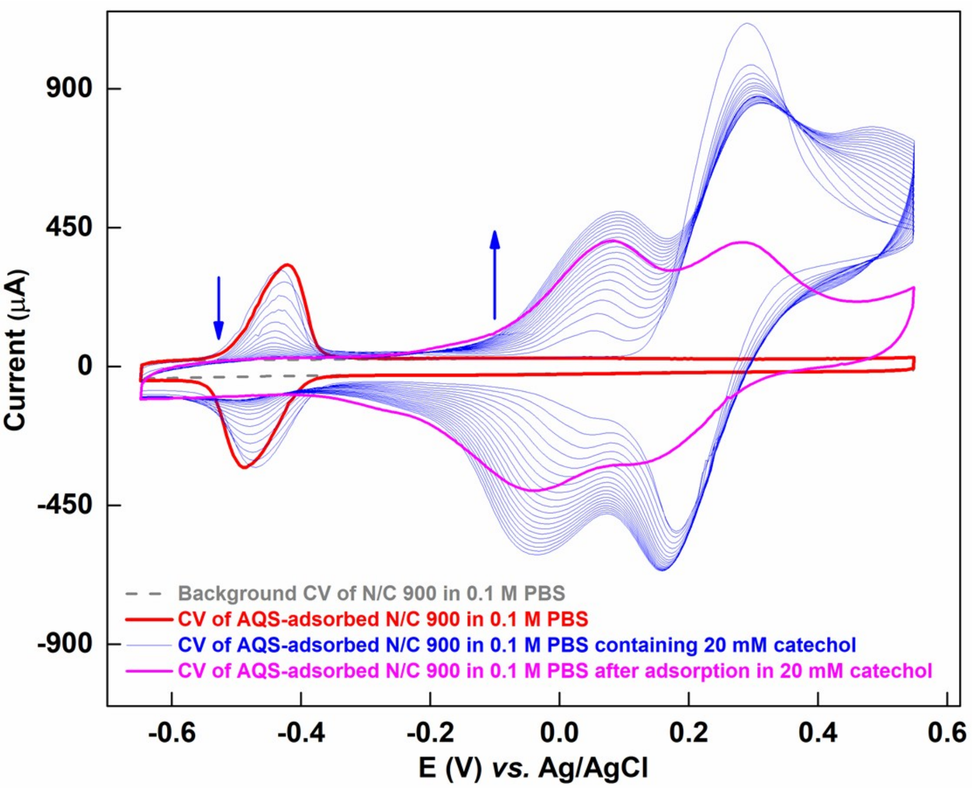

Figure S2 Voltammograms of N/C 900 in argon-saturated 0.1 M PBS (pH 7) at 20 mV s^{-1} scan rate recorded in different conditions. Background CV (gray); AQS-adsorbed electrode (red); potential cycling of AQS-adsorbed electrode in 20 mM catechol (blue); and AQS-adsorbed electrode after catechol adsorption in 20 mM catechol (pink).

The replacement of adsorbed-AQS by oxidized products of catechol on N/C 900 is shown in **Figure S3;** different concentrations of catechol are used for the replacement. Figure S3 (a) shows the voltammogram of N/C 900 catalyst saturated by the adsorbed-AQS; no catechol is used for the replacement of AQS. Figure S3 (b), (c) and (d) show the voltammograms of AQS-adsorbed N/C 900, after potential cycling in 1 mM, 5 mM and 20 mM catechol-containing 0.1 M PBS (pH 7). The reduction in charge of adsorbed-AQS and the respective increment in charge of adsorbed-catechol are tabulated in **Table S2**. With potential cycling in the catechol-free 0.1 M PBS (pH 7), the AQS molecules desorb from the surface at a slow rate; thus, the charge due to adsorbed-AQS on the catalyst surface decreases. **Figure S4** shows the voltammogram of AQS-adsorbed N/C 900 catalyst cycled for 20 times in the catechol-free argon-saturated 0.1 M PBS (pH 7). The charge of AQS-desorption due to 20 potential cycles in catechol-free 0.1 M PBS (pH 7) is accounted as a correction factor (0.14 mC). As the AQS replacement reaction with catechol is performed by 20 potential cycling in argon-saturated 0.1 M PBS (pH 7), 0.14 mC is used to correct the AQS-desorption charge and the same is tabulated in Table 1.

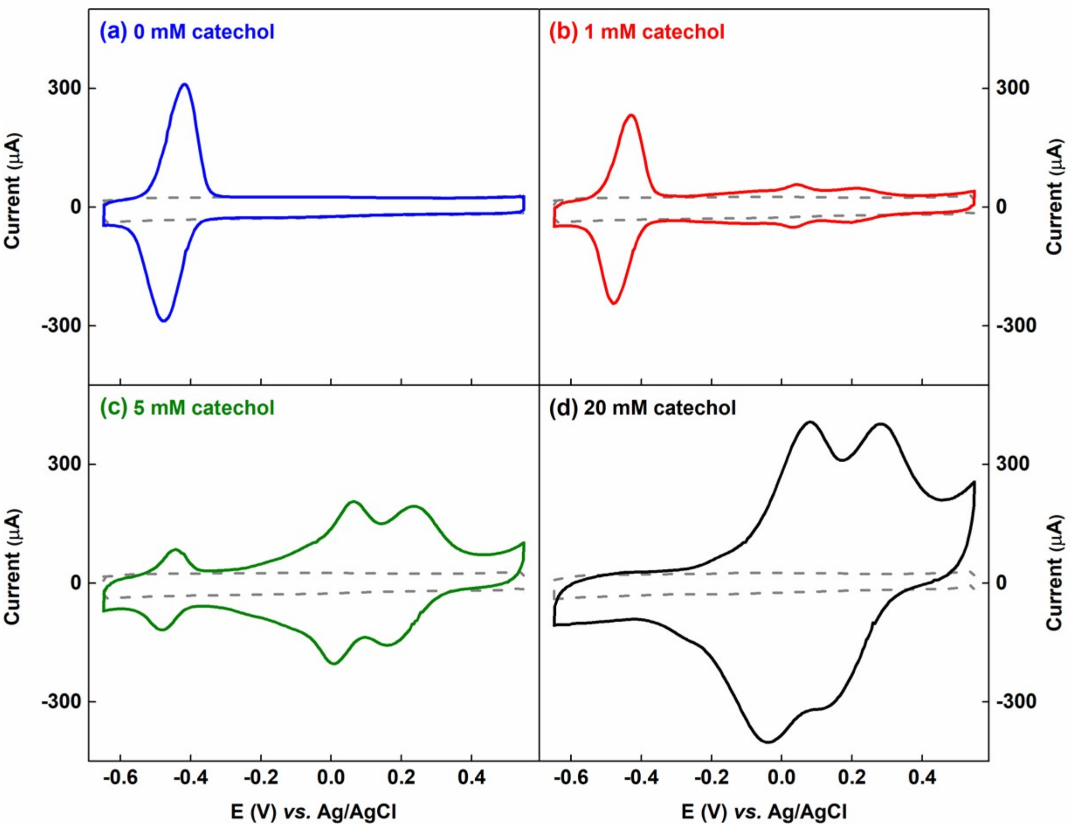

Figure S3 Voltammograms of AQS-adsorbed N/C 900 recorded in argon-saturated 0.1 M PBS (pH 7) at 20 mV s^{-1} scan rate after potential cycling in different catechol concentrations 0 mM (a), 1 mM (b), 5 mM (c), 20 mM (d). Gray dotted line represents the background voltammogarm of N/C 900 recorded in AQS-free argon-saturated 0.1 M PBS (pH 7) at 20 mV s^{-1} scan rate.

From the Table S2, it is observed that the charge due to adsorbed-AQS decreases with increment of the catechol concentration. At 1 mM catechol concentration, the decrement of the adsorbed-AQS charge and the increment of adsorbed-catechol charge is almost comparable; the ratio of the latter to former one is ~1.18. Whereas, after cycling in 5 mM catechol, the ratio is ~2.31. It further increases to ~3.81 while using the 20 mM catechol concentration. It supports the previously proposed conclusion that at higher concentration, the in-situ generated oxidized products of catechol undergo polymerization reaction either with catechol or with the formed oxidized products.[1-3] Thus, at higher concentrations of catechol, it is erroneous to calculate the active site density using the catechol-adsorption method as the polymerization reaction cannot be controlled. Whereas, with AQS-adsorption method, only one saturated adsorption peak is observed in the voltammograms of the AQS-adsorbed catalysts upto 20 mM concentration, and the base of the voltammogram of AQS adsorbed electrode matches with the background one, suggesting no polymerization or unwanted side reactions.

Table S2 Comparison of replacement charge of adsorbed-AQS by adsorbed-catechol on N/C 900

Catechol concentration (mM)	AQS-adsorbed charge (mC) (after background correction)	Reduction in AQS-adsorbed charge (mC)	AQS-adsorbed charge after correction for cycling (mC)	Increment in catechol-adsorbed charge (mC) (after straight line correction)
0	1.40	-	-	0

1	0.94	0.46	0.32	0.38
5	0.26	1.14	1.00	2.34
20	0	1.40	1.26	4.80

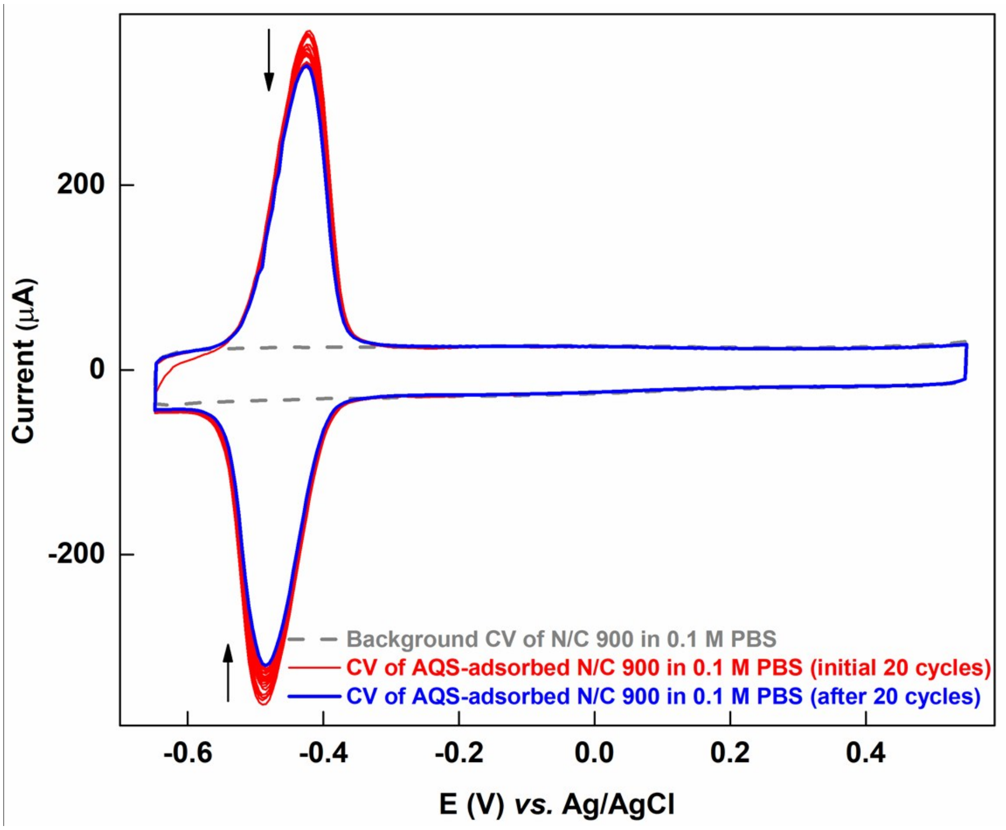

Figure S4 Voltammograms of the AQS-adsorbed N/C 900 (1 mM) cycled in argon-saturated 0.1 M PBS (pH 7) at 20 mV s^{-1} scan rate. Gray line represents the background voltammogarm of N/C 900 recorded in AQS-free argon-saturated 0.1 M PBS (pH 7) at 20 mV s^{-1} scan rate.

Table S3 BET surface area, the surface atomic percentage of nitrogen and oxygen measured from XPS of the catalysts

Catalyst	**A_{BET} (10^4 cm_c^2 g^{-1})**	**N (at %) (From XPS)**	**O (at %) (From XPS)**
C	220	–	1
N/C 700	230	0.60	1.74

N/C 800	270	0.70	1.9
N/C 900	460	1.06	5.48
N/C 1000	515	0.61	14.93
HNO_3 treated C	100	−	11
HNO_3 treated N/C 900	125	1.10	16

Table S4 The double layer capacitance of the nitrogen-doped carbon estimated from the EIS

Catalysts	**Double layer capacitance (C_{dl}) (F g^{-1}) from EIS**
C	5.63
N/C 700	6.39
N/C 800	6.76
N/C 900	21.42
N/C 1000	18.04
HNO_3 treated C	32.77
HNO_3 treated N/C 900	54.77

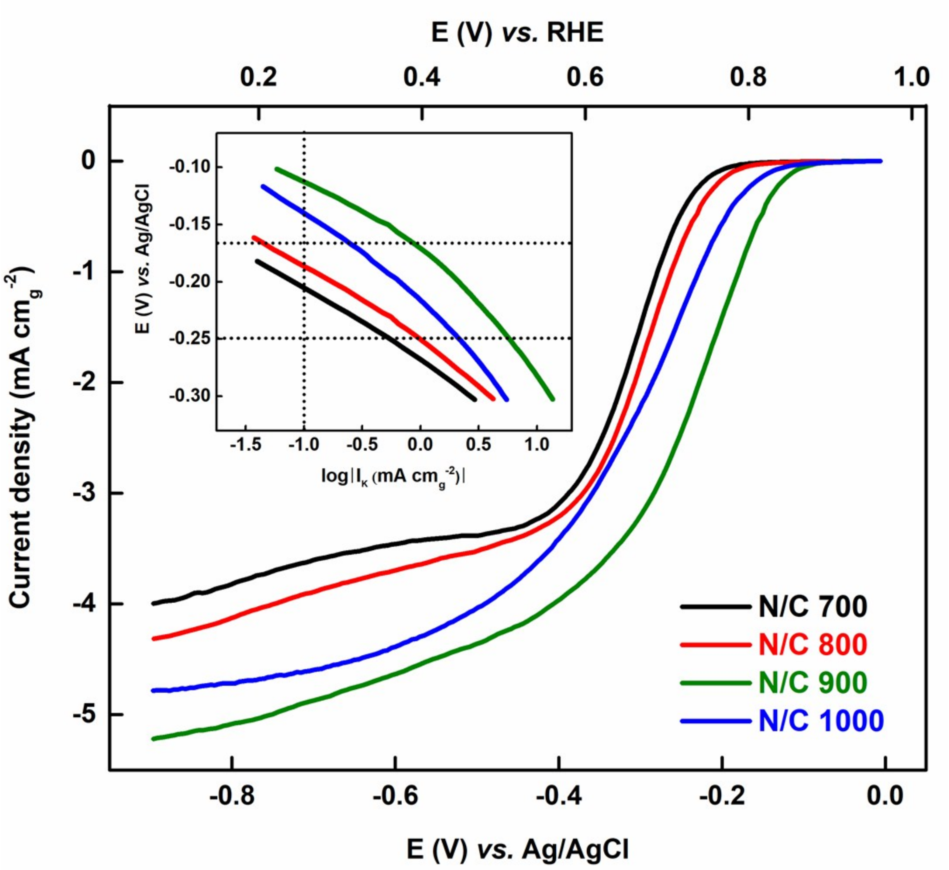

Figure S5 ORR voltammograms of N/C 700, N/C 800, N/C 900 and N/C 1000 in oxygen-saturated 0.1 M KOH solution (pH 13) at a scan rate of 20 mV s^{-1} at 1600 rpm. Inset shows the Tafel plot of the respective catalysts.

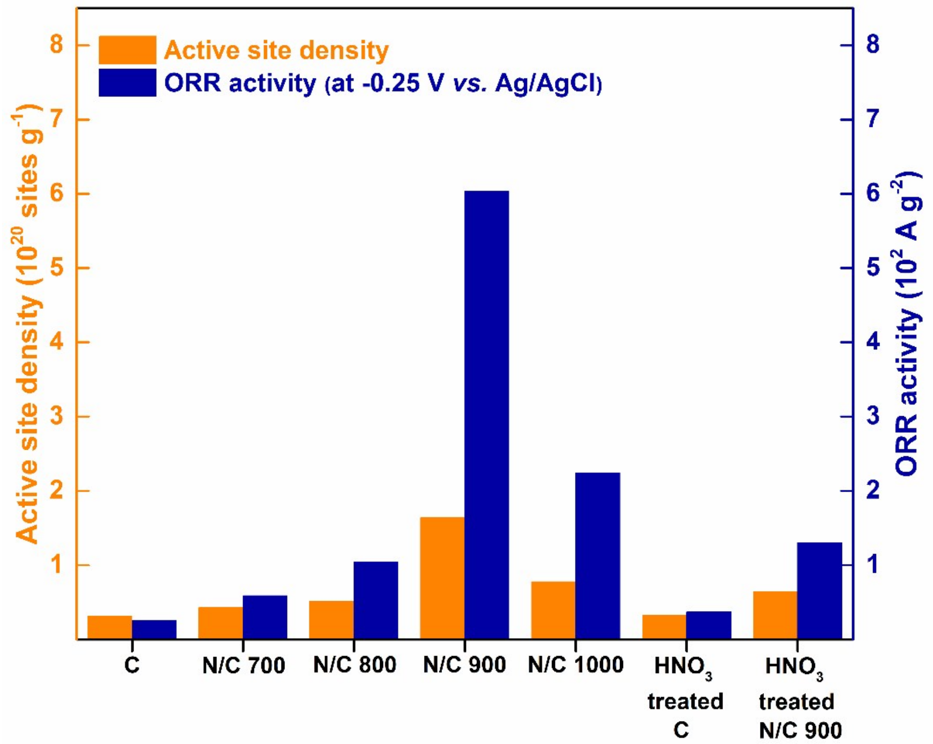

Figure S6 Comparison plot of estimated active site density from AQS adsorption and ORR activity (at −0.25 V vs. Ag/AgCl) of carbon and different functionalized carbon.

References

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