

Supporting Information

Electrochemical estimation of active site density on metal-free nitrogen-doped carbon using catechol as an adsorbate

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S1. Effect of porosity and optimization of catalyst cleaning time

As previously reported by Kanazawa *et al.*, when nitrogen-grafted glassy carbon surface is used for catechol adsorption, negligible amount of catechol is adsorbed on the GCE surface and it can be cleaned by rinsing with water.¹ However, when a high surface area carbon electrode is cycled in the catechol solution, excess amount of bulk catechol may get trapped in the porous structure and it can add to the adsorbed-catechol stripping charge. Therefore, after cycling in catechol solution (adsorbing molecule), all the catalysts are cleaned with water for sufficient time (20 min) to remove the trapped catechol. To further verify that the cleaning time is optimized, the newly prepared carbon catalyst is cycled in 1,4-dihydroxybenzene solution. It is very weak for nucleophilic attack and therefore it does not undergo chemisorption process on the carbon surface, but, can get trapped in the pore volume. Thus, as shown in **Fig. S1**, though the redox peak of 1,4-dihydroquinone centered at ~ 0.05 V is present after 30 sec cleaning in 0.1 M PBS solution (pH 7), it is not present after 20 min. cleaning. Thus, it suggests that 20 min. cleaning is sufficient to remove the pore-volume-trapped adsorbate molecules.

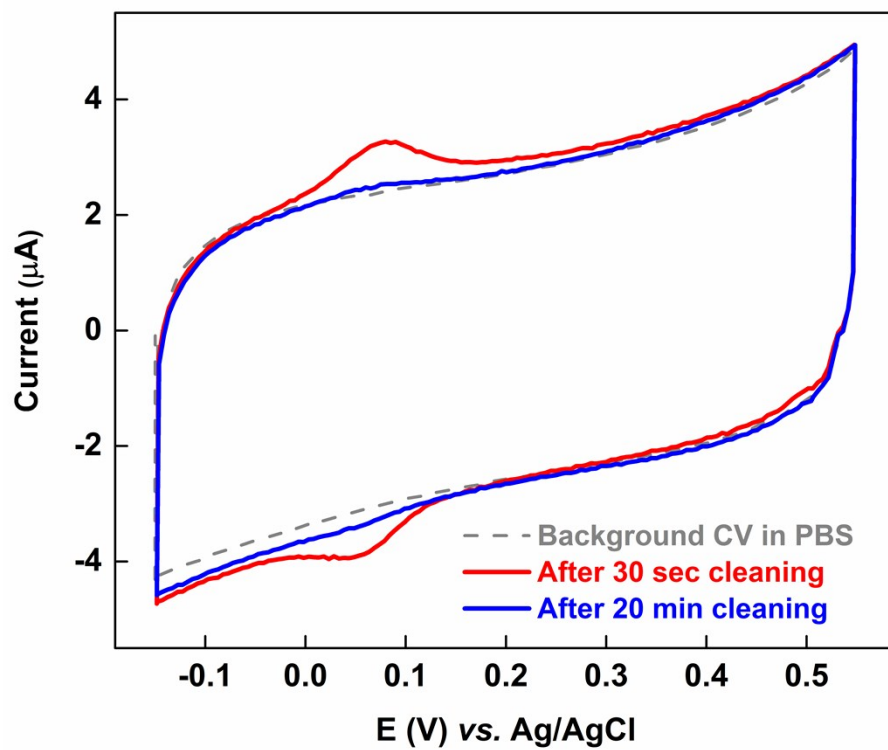


Figure S1 Voltammograms of 1,4-dihydroxybenzene adsorbed KOH treated carbon in argon-saturated 0.1 M PBS solution (pH 7) at 20 mV s^{-1} scan rate.

Table S1 EDR and double layer capacitance values before and after KOH treatment of the nitrogen-doped catalyst.

		R_s (Ω cm ²)	EDR (Ω cm ²)	C (F g ⁻¹)
N/C 700	Before KOH treatment	4.39	~3.6	2.90
	After KOH treatment	4.56	~1.9	6.39
N/C 800	Before KOH treatment	4.76	~3.4	3.83
	After KOH treatment	4.95	~1.8	6.77
N/C 900	Before KOH treatment	3.62	~1.9	9.54
	After KOH treatment	3.78	~1	21.43
N/C 1000	Before KOH treatment	3.68	~2.9	4.57
	After KOH treatment	3.89	~1.4	18.04

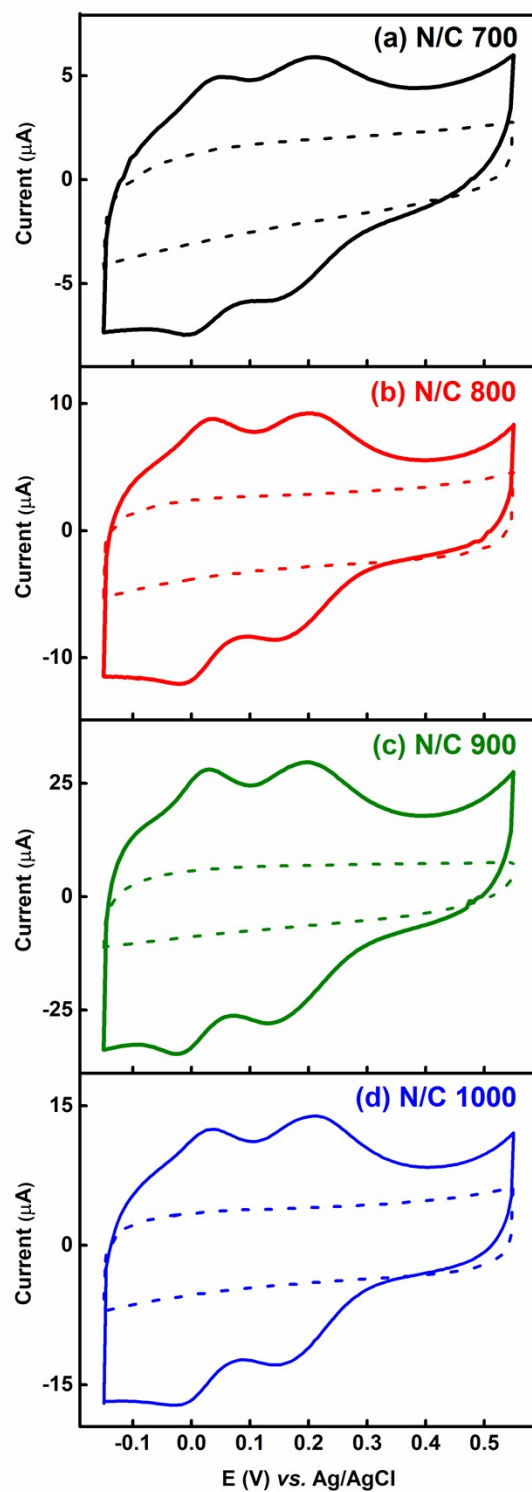


Figure S2 Background and catechol adsorption voltammogram of N/C 700 (a), N/C 800 (b), N/C 900 (c) and (d) N/C 1000 in argon-saturated 0.1 M PBS solution (pH 7) at 20 mV s⁻¹ scan rate.

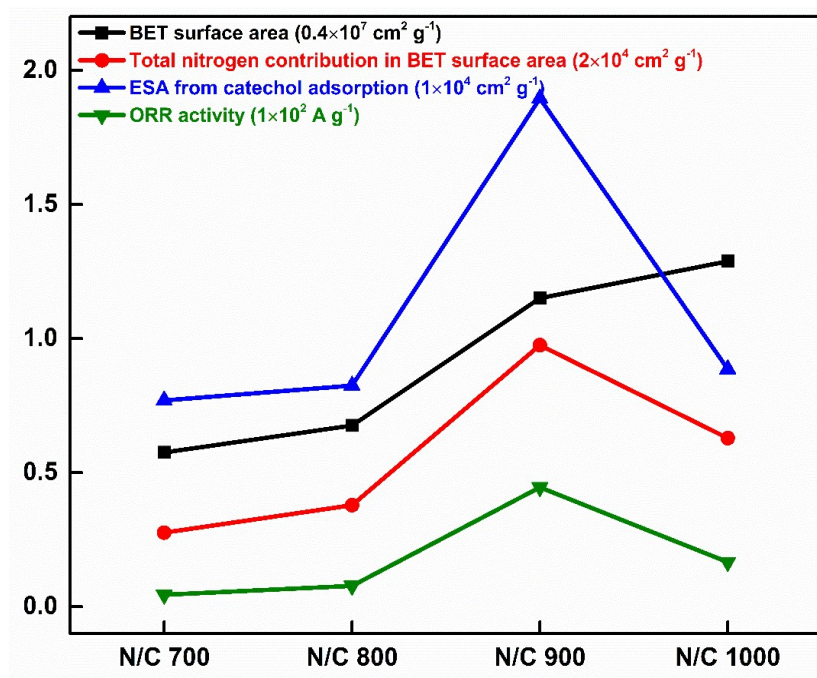


Figure S3 Trends in the ORR activity, BET surface area, nitrogen contribution to BET surface area, and the ESA estimated from catechol adsorption voltammograms of nitrogen-doped carbon samples.

Reference

1. A. Kanazawa, T. Daisaku, T. Okajima, S. Uchiyama, S. Kawauchi, and T. Ohsaka, *Langmuir*, 2014, **30**, 5297–5305.