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Supporting Information

Direct Reduction of Oxygen Gas over Dendritic Carbons with Hierarchical Porosity: Beyond the Diffusion Limitation

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Scheme S1. Proposed transfer path and activation mechanism of oxygen gas discussed in this work. Flooding is an inevitable problem of the cathode in conventional proton-exchange-membrane fuel cells (e.g. Pt/C). The electrode surface was usually wetted by the water droplets (top left), blocking the diffusion of oxygen gas molecules to its surface. The activation of the oxygen molecules, which diffuse to the surface of the electrode, is also limited by the ultra-low concentration of dissolved oxygen (bottom left) as stated in the main text. In contrast, multi-phase activation path (bottom right) achieved by the DBGS electrode could depress possible effect of flooding (top right) and also break the diffusion limitation of oxygen species to give linearly increased ORR current densities with higher work voltages. The unique structure of the DBGS electrode with hierarchical structure and superhydrophobic surface was the key point to maintain such a stable multiphase interface of liquid (water), gas (oxygen gas) and solid (exemplified with graphene in this work) for the direct reduction of oxygen gas bubbles.



Scheme S2. The superhydrophobic electrode obtained from the DNGS catalyst exhibits a Cassie state (a). Parts of the dendrite carbons penetrate into the liquid phase, generating the direct contact of the catalyst with electrolyte for mass and electron transfer (b).



Fig. S1. Dendritic cells in the mammalian immune system. Artistic rendering of the surface of a human dendritic cell illustrating sheet-like processes that fold back onto the membrane surface (from Wikipedia).



Fig. S2. TEM image of CS colloids synthesized through a modified solvothermal method. The average diameter is around 150 nm.



Fig. S3. SEM (a) and TEM (b) images of the CS sample obtained at 900°C under the protection of N_2 flow. Both images show an intensive aggregation without the addition of DCDA.



Fig. S4. SEM (a) and TEM (b) images of carbon sphere aggregation after calcination with urea at 900°C under the protection of N_2 flow. The SEM shows large aggregation of CS instead of well dispersed carbon sphere among graphene layers, which indeed turns out to be "inhomogeneous". Such aggregated morphology is consistent with our zeta potential measurement in Fig. 2b (urea), and thus urea is not a suitable precursor for dendritic carbon synthesis.



Fig. S5. Large-area TEM (a) and SEM (b) images of a typical DNGS sample. Carbon sphere colloids, made from glucose via a hydrothermal method ^[13,14], were selected here as the hard cores to support the graphene layers for constructing dendritic carbon nanostructures via a modified nano-confinement method inside the interlayer space of the as-formed layered $g-C_3N_4$ from DCDA at a temperature around 600 °C, whilst the carbonaceous intermediates generated from the further carbonization of carbon spheres could diffuse into the adjacent interlayer space of the $g-C_3N_4$. Further elevating the synthetic temperature higher than 750 °C could lead to the thermolysis of the layered $g-C_3N_4$ into gaseous molecules and simutaneously liberated the confined carbonceous layers (graphene layers) on the surface of these carbon spheres with improved carbonization degree. This sample was synthesized from the mixture of 40 g DCDA and 480 mg carbon sphere at 900°C under the protection of N₂ flow, which is the best-in-class ORR catalyst for the fabrication of the DNGS electrode. Without special notification, the DNGS sample mentioned in the main text and supporting information was the one presented here.



Fig. S6. TEM images of different batches of the nitrogen-doped graphene (NG) sheets synthesized from calcination of 20 g DCDA and 1 g glucose at 900°C under the protection of N_2 flow.



Fig. S7. XRD patterns of the DNGS (a) and NG (b) samples. Similar broad graphite peaks at around 27° and 44° indicate the formation of tiny graphite domains.



Fig. S8. Nitrogen adsorption-desorption isotherms of the DNGS, NG and CS samples with specific surface areas of 507.45, 545.2 and 118.4 m^2 g⁻¹, respectively.



Fig. S9 XPS N 1s spectra of the DNGS (red) and NG (blue) sample.



Fig. S10. XPS spectrum of the DNGS sample with a N content of 10.7 at.%.



Fig. S11. XPS spectrum of the NG sample with a N content of 10.6 at.%.



Fig. S12. XPS spectrum of the CS sample.



Fig. S13. TEM image of the DNGS-60 sample prepared from 60 mg of CS and 40 g of DCDA at 900°C. Besides the dendritic carbon, additional graphene layers that were not tethered to the surface of the carbon spheres were observed.



Fig. S14. TEM image of the DNGS-120 sample prepared from 120 mg of CS and 40 g of DCDA at 900°C.



Fig. S15. TEM image of the DNGS-240 sample prepared from 240 mg of CS and 40 g of DCDA at 900°C.



Fig. S16. LSV curves of the DNGS samples obtained from the mixture of 480 mg of CS and 40 g of DCDA at different synthetic temperatures. The temperature was optimized to be 900 °C for the synthesis of the DNGS sample to provide the highest current density and the lowest overpotential. All LSV measurements were taken on RDE with a catalyst loading of 0.10 mg cm⁻² in O₂-saturated 0.1 mol L⁻¹ KOH.



Fig. S17. LSV curves of the DNGS samples obtained with different weight ratios of CS and DCDA at 900°C. A tradeoff between the current density and half-wave potential has been made with the 480 mg CS-40 g DCDA-based sample. All LSV measurements were taken on RDE with a catalyst loading of 0.10 mg cm⁻² in O_2 -saturated 0.1 mol L⁻¹ KOH.

Note that both the DCDA/CS ratio and the calcination temperature is optimized through RDE-based linear sweep voltammetry on ORR (Fig. S16-17). We first optimized the components ratio (Fig. S17) from DCDA:CS=40g:60mg (667:1) to DCDA:CS=40g:480mg (83:1) and found its current output gradually increase while the half-wave potential shifts its increasing trend at DCDA:CS=40g:240mg (166:1). Therefore, we made a tradeoff and fixed the ratio DCDA:CS=83:1. Later on, we optimized the calcination temperature from 800°C to 1000°C (Fig. S16). The electrochemical measurements indicate that 900°C calcination has both the highest current output and the highest half-wave potential. As a result, we conclude that the sample prepared with DCDA:CS = 83:1 weight ratio at 900°C is the best sample.



Fig. S18 (a), Linear sweep voltammetry (LSV) curves of DNGS and controlled samples. The halfwave potential of the DNGS electrocatalyst (0.76 V versus RHE) is better than that of CS (0.56 V versus RHE) and NG samples (0.72 V versus RHE). (b), ORR current density of various ORR catalysts on RDE at 0.75V versus RHE. (c), The diffusion-current-corrected Tafel plots of Pt/C (52 mV/decade, black), DNGS (48 mV/decade, red), NG (47mV/decade blue) and CS (43 mV/decade green) samples. (d), The electron transfer number (n) of the DNGS sample as a function of the overpotential. The n values ranged between 3.5 and 4.0 indicate a good selectivity of the DNGS sample for the four-electron pathway of ORR. All measurements were carried out on RDE at 1600 rpm in O₂-saturated 0.1 mol L⁻¹ KOH solution with a sweep rate of 10 mV s⁻¹.



Fig. S19. Electrochemical impedance spectroscopy (EIS) of the DNGS (red), NG (blue) and CS (green) samples in O₂-saturated 0.1M KOH solution. At a low frequency, our DNGS sample showed a much steeper slope as compared to the control samples, indicating a more favorable mass transfer process.



Fig. S20. Temperature programmed desorption results of DNGS and NG samples. The rigid-flexible hybrid structures of the DNGS sample help to stabilize the dendritic structure of the DNGS and keep the tethered graphene layers from aggregation, resulting in more accessible active centers. Considering the poor chemical stability of carbon materials in oxygen-rich atmosphere at higher temperatures for TPD measurements, CO₂ molecules were chosen as the probe for temperature programmed desorption analysis to monitor the amounts of polarized C-N bond, which have been widely accepted as the active centers for ORR in metal-free nanocarbons. Considering the similar doped concentrations of nitrogen atoms (Fig. S10-11) and BET surface areas (Fig. S8) of the DNGS and NG samples, we could attribute the higher and stronger TPD peak of DNGS sample to the formation of more accessible active centers, again due to such a dendritic structure with more stabilized graphene-based network. The role of the dendritic structure in stabilizing the graphene layers in the DNGS sample was further demonstrated by the negligible change in the TPD peak before and after wetting the samples with water. It should be noted that graphene-based monoliths were usually condensed into closely packed aggregation during such a wetting-drying process with a polar solvent as described in the literature, as well as reflected by the obvious loss in the adsorption capacity of the NG sample after the same wetting-drying process in this work (dotted line). Just like the dendritic cell (Fig. S1) being able to keep itself stable in blood, the mechanical stability of DNGS lays a solid foundation for the possible reduction of oxygen gas in a liquid-phase ORR system.



Fig. S21. (a), The photograph of the DNGS electrode prepared via coating the DNGS ink on the carbon fiber paper. The superhydrophobic surface of the DNGS electrode was well reflected by the large contact angle (b) and the lotus effect (Movie S1). (c), The wetted-DNGS electrode was obtained through several cycles of LSV measurements without oxygen flow to consume all absorbed oxygen gas (Movie S2). The removal of all absorbed oxygen gas turns the electrode surface into a hydrophilic one (Movie S3).



Fig. S22. LSV curves of the DNGS electrode (red) and the Pt/C-based electrode (black) obtained via coating the catalyst ink on a 1 cm \times 1cm carbon fiber paper and tested under an oxygen gas flow (0.2 L min⁻¹) in 0.1 mol L⁻¹ KOH solution with a sweep rate of 10 mV s⁻¹. The catalyst loading was 1 mg cm⁻² for all electrodes.



Fig. S23. The LSV curves of the DNGS-electrode, prepared via coating the DNGS ink on the carbon fiber paper, are almost the same when either Pt net (red) or graphite rod (black) were used as the counter electrodes. This result excludes the possibility of leakage of Pt from the counter electrode for significantly improving the ORR performance of the metal-free DNGS electrode. ORR performance was tested in 0.1 mol L⁻¹ phosphate-buffered saline solution under an oxygen gas flow rate of 0.8 L min⁻¹.



Fig. S24. Experiment apparatus setup for measuring the ORR performance of the large-area electrodes, prepared via coating the catalyst ink on the carbon fiber paper, under different flow rates of oxygen gas. The DNGS electrode serves as the working electrode (A), Counter electrode (B) and saturated calomel electrode as the reference electrode (C). Oxygen gas flow is controlled though a flowmeter and bubbled through a glass tube with a sand core at the end (D).



Fig. S25. Ten cycles of LSV measurements over the DNGS electrode, prepared via coating the DNGS ink on the carbon fiber paper, under an oxygen gas flow rate of 0.2 L min⁻¹.

Table S1

No.	Material	Current Density (mA cm ⁻² @0.4V vs RHE)	Slope (mA cm ⁻² /100mV)	Electrolyte	Refs.
1	DNGS	28.5	7.8	0.1M KOH	This Work
2	I-GDE	0.8	2.5	0.1M KOH	[1]
3	N-rGO	18	6.8	0.1M KOH	[2]
4	CQD	8	3.5	0.5M KOH	[3]
5	T-CoNCNT-CFP	23	5.5	0.1M KOH	[4]

Movie S1. Formation of gas layer on the surface of the DNGS electrode. Owing to the superabsorbing nature of the graphene sheets in the DNGS, a gas layer could stay stable on the surface of the DNGS electrode. As a result, water droplets were repelled away from the DNGS electrode surface.

Movie S2. Evidence for the direct activation of oxygen gas for ORR. The surface of DNGS was initially saturated with O_2 bubbles, giving it a silvery appearance, which serves as a finite reservoir of O_2 . During the first cycle of the LSV measurement, the area of the silver gas layer became gradually smaller and finally disappeared in O_2 -saturated 0.1 mol L⁻¹ KOH without an oxygen gas flow. Therefore, the consumption of absorbed gas layer without an additional oxygen gas supply during the LSV test was verified, resulting in a wetted DNGS electrode finally.

Movie S3. The hydrophilic nature of the wetted-DNGS electrode. The surface of the wetted DNGS electrode became hydrophilic, as well reflected by the rapid spreading of water droplets on its surface.

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