Supplementary Information

Size effect of graphene on electrocatalytic activation of oxygen

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Experimental Section

Raw materials: Graphite powder (GP) was purchased from Asbury Carbons Inc. Carbon nanotubes (CNT) were purchased from Chengdu Organic Chemicals Co. Ltd. N-doped carbon nanotubes (NCNT) were synthesized according to the method reported by Bitter et al.^[1] Briefly, 20 wt% Co/SiO₂ catalysts prepared by impregnating porous SiO₂ nanosphere in Co(NO₃)₃ solutions were used for synthesis of NCNT. 8 g catalyst was loaded in a quartz reactor and reduced at 873 °C for 2 h in a 20% H₂/Ar flow (100 mL·min⁻¹). Acetonitrile was carried into the catalyst bed at this temperature by an Ar flow (50 mL·min⁻¹) at 298 K. The product was purified by refluxing sequentially in 1 M KOH, 18% HCl, 10% HF solution and deionized water, followed by drying at 120 °C for 12 h.

Graphene synthesized by ball milling: The ball milling was performed on a QM-3SP2 planetary ball mill. In a typical experiment, 2.0 g precursor materials (GP, CNT or NCNT) and 60 g steel balls (1-1.3 cm in diameter) were put into a hardened steel vial inside a glove box and purged with high purity argon (99.999%) for 20 min before the vials were sealed. The ball milling was carried out at 450 rev. /min for 0.2 h-20 h.

Characterization: Atomic force microscopy (AFM) analysis was conducted in veeco multimode 3D. X-ray diffraction (XRD) patterns were collected on a Rigaku D/MAX

2500 diffractometer with Cu Kα radiation (λ =1.5418 Å) at 40 kV and 200 mA. The scan speed was 5°/min and the step size was 0.02°. During X-ray photoelectron spectroscopy (XPS) measurement, Mg Kα radiation (1253.6 eV) with a power of 200 W and pass energy of 50.0 eV was used. Transmission electron microscopy (TEM) was carried out on a FEI Tecnai F30 microscope and a G² microscope operated at an accelerating voltage of 300 and 120 kV, respectively. The samples were placed onto an ultrathin carbon film supported on a copper grid. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) was conducted in SHIMADZU ICPS-8100. The samples for ICP-AES analysis was first heated at 850 °C for 2 h in air, followed by treatment in HCl. Raman spectroscopy was performed on a Jobin Yvon LabRAM HR 800 instrument with a 532 nm excitation laser at a power of around 1 mW.

Oxygen reduction reaction (ORR) activity: The ORR activity was evaluated on a 2273 potentiostat/galvanostat equipped with a three-electrode electrochemical cell and gas flow controlling systems. Mercury/mercuric oxide electrode (Hg/HgO) (1 M NaOH-filled) or Ag/AgCl (saturated KCl-filled) was used as the reference electrode, and a Pt-foil as the counter electrode. A glassy carbon rotating ring disk electrode with a diameter of 5 mm covered by a thin film of the catalyst was used as the working electrode. Typically, 5 mg catalyst was ultrasonically suspended in 2 mL ethanol and 50 μ L of Nafion solution (5wt. %, Du Pont) to form a homogeneous ink. Then 25 μ L of the ink was spread onto the surface of the glassy carbon with a micropipette followed by drying under room temperature. Experiments were conducted either under alkaline conditions (1 M NaOH solution) or acidic conditions (0.1 M H₂SO₄ solution), which were saturated with oxygen at 25 °C. A rotation rate of 2500 rpm and a sweep rate of 10 mV·s⁻¹ were employed.



Figure S1. a) TEM image of GP. b-c) HRTEM images of graphene nanosheets in GP-BM obtained from ball milling of GP for 20 h.



Figure S2. XRD patterns of GP, CNT, NCNT and their resulting products via ball milling for 20 h.



Figure S3. N₂ adsorption-desorption isotherms of GP, CNT, NCNT and their resulting products (GP-BM, CNT-BM and NCNT-BM) via ball milling for 20 h.

Sample	BET surface area $(m^2 g^{-1})$	
GP	3.9	
GP-BM	905	
CNT	208	
CNT-BM	642	
NCNT	150	
NCNT-BM	620	

Table S1. Surface areas of GP, CNT, NCNT and corresponding products GP-BM, CNT-BM and NCNT-BM via ball milling for 20 h.



Figure S4. Raman spectra for graphene GP-BM, CNT-BM, and NCNT-BM obtained via ball milling for 20 h and their parent materials GP, CNT and NCNT in comparison with XC-72.



Figure S5. TEM images at different magnifications: a)-b) CNT, and c)-d) CNT-BM obtained via ball milling for 20 h.



Figure S6. TEM images at different magnifications: a)-b) NCNT, and c)-d) NCNT-BM obtained via ball milling for 20 h.



Figure S7. XPS spectra (a) wide spectra of nanographene via ball milling for 20 h and their parent materials; (b) N1s spectra of NCNT and NCNT-BM and their fitting, which indicate the presence of mainly three types of nitrogen species: graphitic (green), pyridinic (blue) and pyrrolic N (red).

Sample	С	0	Graphitic\Pyridinic\
	(at. %)	(at. %)	Pyrrolic N (at. %)
GP	97.6	2.4	
GP-BM	91.4	8.6	
CNT	97.7	2.3	
CNT-BM	86.9	13.1	
NCNT	91.6	4.4	4.0 (1.2\1.1\1.7)
NCNT-BM	86.6	9.9	3.5 (1.0\0.4\2.1)

Table S2. Chemical compositions of GP, CNT, NCNT and their resulting products via ball milling for 20 h, estimated from XPS measurements.



Figure S8. Electroactivity of graphene resulting from GP, CNTand NCNT via ball milling for 20 h in comparison to XC-72 and commercial 40% Pt-C/GC. From top to bottom, the curves correspond to GP, CNT, XC-72, GP-BM, CNT-BM, NCNT, NCNT-BM and 40%Pt/C. All tests have been carried out in O_2 -saturated 0.1 M H₂SO₄ at a rotation rate of 2500 rpm and the scan rate of 10 mV·s⁻¹. Before measurements, the samples were repeatedly swept from -0.2 to 0.8 V in an N₂-protected 0.1 M H₂SO₄ until a steady voltammogram curve had been obtained.

DFT Calculation

All the electronic structure calculations were performed using the Vienna Ab-initio Simulation Package (VASP) with the projector augmented wave method and a cutoff energy of 400 eV.^[2-8] The generalized gradient approximation method with Perdew-Burke-Ernzerhof (PBE) functional for the exchange-correlation term^[9,10] and a Gaussian smearing with a value of σ of 0.05 eV were used. The graphene edges are simulated in nanoribbon models, as shown in Figure S9-10. The models were set in rectangular supercells. The vacuum thickness in the directions perpendicular and parallel to the ribbon plane was set to 10 and 9 Å, respectively. The armchair and zigzag edges were built by replicating 3 and 6 times the bare ribbon unit cell along the ribbon axis direction, respectively (Figure S9-10). The nanoribbon with armchair and zigzag edges consists of 6 and 5 benzene rings in width, respectively. A wider ribbon

model was tested and showed negligible effect on results. A $4 \times 1 \times 1$ Monkhorst-Pack **k**-point sampling was used for all models.^[11] Spin-polarization was considered for both edges. The convergence of energy and forces were set to 1×10^{-4} eV and 0.03 eV/Å, respectively.

The effect of water was considered in the free energy profile of the reaction by adding a correction on the formation energy of reaction intermediates due to the water effect. In our previous DFT study of ORR mechanism on N-doped graphene, the water effect was well quantified under the reaction conditions similar to the current system.^[12] Moreover, the active sites in the two systems are all carbon atoms of the graphene network. Therefore, we suggest that the water effect is similar in the two systems and here we used the data obtained from the previous work for water effect.

At 298 K with the electropotential 0 V and pH = 0, the reaction $^{1}/_{2}$ H₂(1atm) \rightarrow H⁺ $+ e^{-}$ is in equilibrium. By referring the potential to that of the normal hydrogen electrode we can use the free energy of $\frac{1}{2}$ H₂ (1atm) instead of that of H⁺(1M) + e⁻, upon which the free energy of $H^+(10^{-14}M) + e^-$ can be obtained by adding a correction of energy in pH: $\Delta G(pH) = kT \ln[H^+] = -pH \cdot kT \ln 10$, where pH = 14.^[13] The effect of a bias was included for all the states that involve electron transfer in the reactions by adding a shift on the free energy: $\Delta G(U) = neU$, where n is number of electrons transferred and U is the electrode potential.^[13] In our calculations, we used U = 0.04V (vs. NHE) from cyclic voltammetry results. The free energies of the intermediates were obtained by $G = E_{total} + ZPE - TS$, where E_{total} is the total energy of species, ZPE is the zero point energy and S is the entropy. The free energy of H₂O in bulk water was calculated in the gas phase with a pressure of 0.035 bar, which is the equilibrium vapor pressure of H₂O at 298 K. The free energy of O₂ was derived as $G(O_2) = 2G(H_2O) - 2G(H_2) - 4.92$ eV from the free energy change of the reaction O_2 $+ 2H_2 \rightarrow 2H_2O$ which is 4.92 eV under the standard condition. The free energy of OH ⁻ was derived as $G(OH^{-}) = G(H_2O) - G(H^{+})$ because the reaction $H^{+} + OH^{-} \rightarrow H_2O$ is in equilibrium in water solution. In this study, the entropies of molecules in the gas phase were obtained from the literature.^[14]

The transition state (TS) of each elementary reaction was searched using the

constrained minimization approach^[15-17] in the presence of water molecules according to the following procedure: (i) Several layers of water with the density of 1 g/cm³ were placed above the surface and then molecular dynamics (MD) calculations were carried out for ~25 ps; (ii) at least six structures selected from MD calculations were optimized and the most stable structure was obtained; and (iii) the TS was searched in the most stable structure. In electrochemical systems, reactions occur usually on charged electrodes. To consider the charges, the approach (ii) in Ref ^[12] was used to calculate the TS, which was approved to be an efficient and reliable method. The calculating procedure is as follows:

We first located the TS of each reaction step on the edge site without charge. The work function (Φ) of each TS was calculated and adjusted to the correct value according to U (equation 1) by adding electrons into the system. Then, each TS was refined in the charged system. The change of Φ due to this refinement was neglected because of the very small structure change. The initial state (IS) of each reaction step was determined with the same charge as that of the corresponding TS. A compensating background charge was distributed homogenously over the unit cell to maintain overall charge neutrality which is a common approach implemented in VASP. The electrode potential U was obtained by referring the work function Φ of the system to the absolute potential of NHE (U_{NHE}) via the following equation

$$U = 0.04 \text{ V} = \Phi/e - U_{\text{NHE}}$$
(1)

where 0.04 V is the experimental onset potential. The value of $U_{\rm NHE}$ has been reported in the range from 4.44 to 4.85 V.^[18-21] Our calculations show that an uncertainty of ~0.20 V on the electropotential causes an error of ~0.03 eV on the reaction barrier. Therefore, we used 4.65 V for $U_{\rm NHE}$, expecting no significant effect on our results. Φ was calculated by adding a thin (~3 Å) vacuum layer above the water layers, as proposed by Filhol and Neurock.^[22] More details in thermodynamic method can be found in Ref^[12].

The free energy profiles of the evolution of -COOH, -OH and -CHO on zigzag edges are shown in Figure S11. The reaction pathway is illustrated in Scheme S1.



Scheme S1. Reaction scheme of the evolution of (1) –COOH , –OH and (2) –CHO on zigzag edges. It should be noted that we use small molecules (CO₂, HCOOH) rather than ions (CO₃²⁻, HCOO⁻) as the products considering the restriction in computational method. In alkaline solution, the chemical potential of CO₂ and HCOOH is even lower. Therefore, the reactions should be more exothermic than illustrated in Figure S11.

Under the experimental conditions (pH=14 and U=0.04V vs. NHE), these reaction steps above mentioned are strongly exothermic with activation barriers no more than 0.3 eV according to our DFT calculations. This suggests that these reactions can readily occur.

On zigzag edge that is fully saturated with H the edge site is in a coverage of 1/2 monolayer under reaction conditions. The energy profile on this edge is calculated under this coverage.



Figure S9. Supercells of nanoribbon with zigzag edges containing frequently observed oxygen-containing groups. From left to right: nanoribbon fully saturated by

H, nanoribbons with -OH, C-O-C, C=O, -CHO, -COOH. The white, grey, and red spheres represent H ,C, and O atoms, respectively.



Figure S10. Supercells of nanoribbon with armchair edges containing frequently observed oxygen-containing groups. From left to right: nanoribbon fully saturated by H, nanoribbons with -OH, $C-O-C^1$, $C-O-C^2$, C=O, -CHO, -COOH. The white, grey, and red spheres represent H ,C, and O atoms, respectively.



Figure S11. Calculated evolution of oxygen-containing groups at the zigzag edge of graphene under experimental conditions. a) –COOH and –OH and b) –CHO will be transformed into C=O. The grey, red and white balls represent C, O and H atoms, respectively.

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