Supporting Information

Structure-Controlled Graphene Electrocatalysts for High-Performance H₂O₂ Production[†]

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Experimental Section

Materials

Potassium hydroxide (KOH, \geq 99.99%), hydrogen peroxide solution (H₂O₂, 30% in H₂O), potassium ferricyanide (III) (K₃Fe(CN)₆, 99%), ethylenediaminetetraacetic acid (EDTA, \geq 98.0%), cerium sulfate (Ce(SO₄)₂, \geq 99.99%), potassium persulfate (K₂S₂O₈, \geq 99.0%), phosphorus pentoxide (P₂O₅, \geq 98.0%), sulfuric acid (H₂SO₄, \geq 95-98.0%), potassium permanganate (KMnO₄, \geq 99.0%), and hydrochloric acid (HCl, 37%) were obtained from Sigma-Aldrich. The Nafion 117 membrane was purchased from Fuel Cell Store.

Synthesis of graphene oxide

Graphene oxide (GO) was synthesized using the modified Hummer's method.¹ Graphite powder (1 g), $K_2S_2O_8(0.5 \text{ g})$, and $P_2O_5(0.5 \text{ g})$ were mixed in H_2SO_4 solution (4 mL) at 80 °C for 4.5 h. The suspension was washed 6 times with deionized water and air-dried overnight to obtain pre-oxidized graphite samples. KMnO₄ (3 g) was added slowly to the pre-oxidized graphite powder and H_2SO_4 (23 mL) mixture at 0 °C. The suspension was then stirred at 36 °C for 2 h. After adding deionized water (46 mL) to the solution at 0 °C, the suspension was vigorously stirred again at 36 °C for 2 h. For oxidation, H_2O_2 solution (2.5 mL) and ultrapure water (140 mL) were added. Finally, the dark brown color of the GO solution was obtained by washing with deionized water and filtering with HCl (250 mL). The GO solution was dialyzed for 2 weeks and collected through sonication for 1.5 h.

Synthesis of 3D crumpled graphene oxide

Crumpled graphene was synthesized using an aerosol spray drying process.² GO droplets were formed from the GO solution with an ultrasonic nebulizer. The GO droplets were passed through a heated furnace with Argon gas at a flow rate of 1 L min⁻¹. The accumulated GO sheets rapidly shrunk and formed 3D structures by capillary force due to the evaporation of water droplets on the surface. The OCG particles were collected on a polycarbonate filter

connected to the end of the furnace tube and vacuum pump. The OCG-250, OCG-500, OCG-800, and OCG-1000 samples were synthesized at reduction temperatures of 250, 500, 800, and 1000°C.

Material characterization

Morphology was analyzed with transmission electron microscopy (TEM, HD-2700, FEI Tecnai F30, and Hitachi HT-7700) and scanning electron microscopy (SEM, Hitachi SU8230) images. Raman spectroscopy (Renishaw Raman Spectrometer-Vis/near-IR) and X-ray diffraction (XRD, X-Pert Pro alpha-1) verified the structural changes in the OCGs. X-ray photoelectron spectroscopy (XPS, Thermal K-Alpha XPS) and Fourier-transform infrared spectroscopy (FT-IR, Nicolet 6700 FT-IR) were employed to investigate the chemical structure and composition. High-resolution XPS C1s and O1s peaks were fitted using XPSPEAKS 4.1.

Electrochemical characterization

Electrochemical testing was conducted using a rotating ring disk electrode (RRDE) experimental setup (Pine Instruments Corporation) with a standard three-electrode electrochemical cell. A graphite rod and Ag/AgCl (saturated potassium chloride) were used as the counter and reference electrodes, respectively. All potentials were converted to a reversible hydrogen electrode (RHE). 0.5 mg of catalyst powder and 50 μ L of a 5 wt% Nafion solution (1100 EW, DuPont) were dissolved in 1.25 mL of D.I. water and 1.25 mL of isopropyl alcohol. After ultrasonication of the mixture for 30 min to obtain a homogeneous suspension, 10 μ L of ink was drop-cast onto a glassy carbon electrode (GCE). The catalyst loading density of all the catalysts on the GCEs was 10 μ g cm⁻², and the thin films on the surfaces of the GCEs were dried under ambient conditions. The electrochemical surface cleaning process was performed before obtaining all electrochemical data via 100 voltage-cycling tests from 0.05 to 1.0 V vs. RHE at a scan rate of 100 mV s⁻¹ in an Ar-saturated 0.1 M KOH electrolyte. After stabilizing the cyclic voltammogram curves, we performed linear sweep voltammetry (LSV) in O₂-

saturated 0.1M KOH electrolyte by rotating the shaft of the working electrode at 1600 rpm. The potential sweeps started at 0.2 V vs. RHE and repeated in a potential range of 0.05 to 1.0 V vs. RHE with a scan rate of 10 mV s⁻¹ while holding ring potential at 1.2 V vs. RHE. The potentials vs. Ag/AgCl were converted to the reversible hydrogen electrode (RHE) using the Nernst equation: $E_{RHE} = E_{Ag/AgCl} + 0.198 + 0.059 \times \text{pH}$ (pH = 13 for 0.1 M KOH and pH = 7 for 0.5 M NaCl). All current densities were normalized to the area of the disk electrode.

The ring collection efficiency (*N*) was measured using 2 mM $K_3Fe(CN)_6$ in a 0.1 M KOH electrolyte. A bare glassy carbon RRDE was used for measuring. The LSV curves were collected by sweeping potential from 0.1 to 1.4 V vs. RHE, while holding the ring potential at 1.55 V vs. RHE and changing rpm (400, 900, 1600, and 2500). Based on the ratio of the ring current to the disk current, the empirically determined N is 0.25. H_2O_2 selectivity was calculated using the following equation (S1), where I_{ring} is the ring current and I_{disk} is the disk current. The kinetic current was determined using equations S2 and S3, where $I_{l, peroxide}$ was from the highest current value in the potential range. The total electron transfer number (n) for the ORR was calculated using equation (S4).

$$H_2O_2 \text{ selectivity (\%)} = 200 \times (I_{ring}/N)/(I_{disk}+I_{ring}/N)$$
(S1)

$$1/I_{\text{peroxide}} = 1/I_{l, \text{ peroxide}} + 1/I_{k, \text{ peroxide}}$$
 (S2)

$$I_{\text{peroxide}} = I_{\text{ring}} / N \tag{S3}$$

$$n = 4 \times I_{disk} / (I_{disk} + I_{ring} / N)$$
(S4)

Electrolysis testing was conducted with a H-type electrolytic cell separated by a Nafion 117 membrane connected to an electrochemical workstation. For pre-treatment, the Nafion membrane was boiled in three different solutions (3% H₂O₂ in ultrapure water for 1 h, ultrapure water for 2 h, and 0.5 M H₂SO₄ solution for 1 h, sequentially). The membrane was thoroughly rinsed with ultrapure water several times to remove residue. The working electrode was prepared by a spray-coating method using carbon paper as substrate. The working electrode

and Ag/AgCl reference electrode were placed in a cathode chamber. A graphite rod was used as the counter electrode and placed in the anode chamber. All catalyst loading of the working electrode was fixed at ~0.8 mg cm⁻². A catalyst loading of ~1.2 mg cm⁻² was used for the current density-dependent ORR performance test of OCG-800 on carbon paper electrodes. The 0.1 M KOH electrolyte was evenly distributed in both the cathode and anode compartments under an Ar environment. The total H-cell volume is 50 mL. The 20 mL of 0.1 M KOH electrolyte was evenly distributed to the cathode and anode chamber, and 10 mM of EDTA was added into the only cathode chamber for peroxide concentration measurement. Chronoamperometry (CA) was performed at an applied potential of 0.4 V vs. RHE over 1 h, 2 h, 3 h, and 4 h. The electrolysis of all OCG catalysts was fixed at 0.4 $\mathrm{V}_{\mathrm{RHE}}$ and represented the current density (~40 mA cm⁻²). The stability of the OCG-800 sample was measured after continuous 46 h operation at 0.4 V vs. RHE electrolysis in 0.1 M KOH including 10 mM of EDTA (stabilizer) under an Ar environment. Chronopotentiometry tests were conducted for 4 h each at different current densities of 10, 20, 40, and 60 mA cm⁻² in the H-cell. A titration technique, using an ultraviolet-visible (UV-Vis) spectrophotometer, was used to quantify the H₂O₂ concentration. A standard Ce(SO₄)₂ solution was prepared by dissolving 33.2 mg of Ce(SO₄)₂ in 100 mL of 0.5 M H₂SO₄ solution. The initial color of the solution was yellow by Ce^{4+} ions, but the H_2O_2 reduced Ce^{4+} to Ce^{3+} , which is a colorless solution. After each electrolysis for all catalysts, under a constant potential (0.4 V_{RHE}) for 1, 2, 3, and 4 h, the peroxide concentrations were estimated by extracting a small volume of electrolyte. The extracted electrolytes were appropriately diluted to match the linear interpolation. Absorption intensities at a wavelength of 317 nm were measured using different concentrations of titration H₂O₂ solution. The calibration curves showed good linearity between absorbance and concentration, and all samples were properly diluted to match each calibration curve.

Computational details

First-principles density functional theory (DFT) calculations were performed using the Vienna ab-initio simulation package (VASP).³⁻⁶ The projector augmented-wave pseudopotential method was used to consider the frozen core electrons, and the generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof functional was employed to describe the exchange and correlation effects.^{7, 8} A plane-wave cutoff energy was set to 500 eV. Geometric optimization continued until the total energy difference of the system converged to within 10^{-5} eV, and the maximum force acting on each atom was less than 0.02 eV/Å. Spin-polarized calculations were performed with a gamma-centered grid of 4 × 4 × 1 (for basal), 4 × 1 × 1 (for zigzag edge), and 1 × 4 × 1 (for armchair edge) to integrate the Brillouin zone. For the basal systems, functional groups and defects were modeled based on a rectangular unit cell with 72 carbon atoms. The free energy was calculated by correcting the zero-point energy and entropy from the DFT energy. The corrected values from the previous study were +0.05 eV, +0.35 eV and +0.40 eV for O*, OH* and OOH*, respectively.⁹ Corrections for water solvent effects of OH* and OOH* corresponding to 0.3 eV were included.¹⁰



Figure S1. Schematic illustration of the synthesis process for OCG particles.



Figure S2. SEM (Inset: size distribution of the particles) and TEM images of (a, b) OCG-250, (c, d) OCG-500, and (e, f) OCG-1000.



2 theta (degree) Figure S3. XRD patterns of OCG particles synthesized at different reduction temperatures.



Figure S4. FTIR of as-synthesized OCG particles at different temperatures.



Figure S5. Cyclic voltammetry (CV) scans of (a) OCG-250, (b) OCG-500, (c) OCG-800, and (d) OCG-1000 in the capacitance region at different scan rates under Ar-saturated 0.1 M KOH electrolyte.



Figure S6. Electrochemical surface area measurement of OCG-250, OCG-500, OCG-800, and OCG-1000. The capacitance current densities $((J_{anodic}-J_{cathodic})/2)$ were measured at 0.9 V_{RHE} as a function of scan rate.



Figure S7. (a) Polarization curves of a bare glassy carbon RRDE with a Pt ring in 0.1 M KOH with 2 mM $K_3Fe(CN)_6$ electrolyte at different rotating speeds. The scan rate was 20 mV s⁻¹ and the holding potential of the ring was 1.55 V_{RHE} . (b) Linear fitted curve of the diffusion current densities obtained from the ring and the disk electrode at different rotating speeds. The determined collection efficiency (N) was 0.25.



Figure S8. Linear sweep voltammetry (LSV) curves of (a) OCG-250, (b) OCG-500, (c) OCG-800, and (d) OCG-1000 at different rotating rates in O_2 -saturated 0.1 M KOH electrolyte (Inset: K-L plots at different potentials of 0.5 V and 0.6 V vs RHE).



Figure S9. Comparison plots of OCG catalysts in terms of average H_2O_2 selectivity, ECSA, O1s atomic %, and A_G/A_D ratio.



Figure S10. (a) ORR polarization curves showing the disk and ring current densities, (b) calculated H_2O_2 selectivity, and (c) electron transfer number (n) with different loading amounts of 5, 10, 20, and 50 µg cm⁻² for the OCG-800 catalyst in O₂-saturated 0.1 M KOH electrolyte.



Figure S11. (a) ORR polarization curves showing the disk and ring current densities, (b) calculated H_2O_2 selectivity of the OCG-800 catalyst in O_2 -saturated 0.5 M NaCl electrolyte.



Figure S12. The different concentrations of H_2O_2 in standard ceric sulfate solution, $Ce(SO_4)_2$, were measured by UV-Vis spectroscopy (317 nm). The absorbance-concentration calibration curves were obtained.



Figure S13. SEM and TEM image analysis of the OCG-800 electrode (a, c) before and (b, d) after the stability test. (e) Raman spectra and (f) XRD patterns of the OCG-800 electrode before and after the stability test.



Figure S14. (a) Polarization curve (without IR-compensation) of OCG-800 in O₂-saturated 0.1 M KOH under the H-cell configuration (electrode surface area was $\sim 1 \text{ cm}^2$). (b) V-t curve under different current densities from 10 mA cm⁻² to 60 mA cm⁻² in the H-cell (30 min stabilization time before the change of the current density).



Figure S15. Model systems of the functional groups examined in this study. Black and red circles indicate the active site of the C-O-C type (including epoxide) and the other functional groups, respectively. Gray, red, and white balls denote C, O, and H atoms, respectively.



Figure S16. DFT results of structural changes after oxygen adsorption for (a) C-O-C basal 1 (V_C), (b) C=O basal 1, and (c) C-O-C/C=O basal 2, respectively.





Figure S18. Free energy diagram of ORR on (a) C=O edge 1 and (b) C-O-C basal 1 ($3V_C$) at 0.0 V and 0.7 V vs. RHE, respectively.

Catalyst	O _I (%)	O _{II} (%)	O _{III} (%)	O _{IV} (%)
OCG-250	3.7	27.2	1.7	0
OCG-500	4.5	4.5	7.5	1.6
OCG-800	4.1	3.8	2.3	0.9
OCG-1000	2.1	2.5	4.4	0.8

 Table S1. Atomic percentages of oxygen species in OCG particles.

Catalyst	RRDE Selectivity	Loading amount / Electrode area	Operating condition H-cell, 0.1 M	H_2O_2 productivity (mmol g _{Catal} ⁻¹ h ⁻¹)	Ref.
OCG 800	92~100% @ 0.05 to 0.7 V _{RHE}	0.78 mg cm ⁻²	KOH + 10 mM EDTA, 0.4 V _{RHE}	473.9 (±29)	This work
O-CNTs	~90% @ 0.7 V _{RHE}	~2 mg cm ⁻²	H-cell, 1 M KOH, ~20 mA cm ⁻²	111.7	11
Hierarchically porous carbon	95~70.2%	0.6 mg cm ⁻² , 7.5 cm ²	H-cell, pH 1-7, -0.5 V _{SCE}	395.7-110.2	12
oxo-G	>82% @ 0.1 to 0.6 V _{RHE}	0.1 mg cm ⁻²	H-cell, 0.1 M KOH, 0.2 V _{RHE}	224.8	13
Co ₁ -NG(O)	~82% @ 0.1 V _{RHE}	1 mg cm ⁻²	H-cell, 0.1 M KOH + 10 mM EDTA, 50 mA	418 (±19)	14
Fe-CNT (single atom)	>95% @ 0.822 V _{RHE}	0.5 mg cm ⁻² / 2.5 cm ²	H-cell, 1 M KOH, 43 mA cm ⁻²	1600	15
Partially oxidized Pd on oxygen- functionalized CNTs	95-98% @ 0.3 to 0.7 V _{RHE}	0.1 mg cm ⁻²	H-cell, acidic electrolyte, 10mA cm ⁻² at 0.1V	1701	16

Table S2. Summary of previously reported catalysts for H_2O_2 production.

Model	*	O*	OOH*	Model	*	O*	OOH*
C-O-C basal 1 (V _C)	-656.39783	-661.12217	-669.81595	C-O-C edge 1	-419.91768	-425.82857	-434.03919
C-O-C basal 1 (2V _C)	-650.34472	-656.18293	-664.25717	C=O edge 1	-486.39862	-490.96169	-500.44148
C-O-C basal 1 (3V _C)	-643.99626	-649.98422	-658.14103	C=O edge 2	-429.16226	-433.33762	-442.77566
C-O-C basal 2	-658.75236	-663.60365	-672.59594	OH basal	-668.35503	-672.97250	-682.32842
C-O-C basal 3	-643.06177	-649.10721	-657.33153	OH edge	-487.68700	-492.87585	-502.18476
C=O basal 1	-666.61466	-671.32797	-680.75956	COOH edge	-503.60945	-508.44421	-517.80717
C=O basal 2	-658.75236	-663.24633	-672.60375	epoxide	-668.04296	-672.25499	-681.05771
C=O basal 3	-663.65365	-668.08961	-677.57252				

Table S3. Calculated DFT energies with zero-point energy, entropy and solvation effect correction.

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