Supporting Information for

Intrinsic Relationship between Enhanced Oxygen Reduction Reaction Activity and Nanoscale Work Function of Doped Carbons

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Experimental Section

Synthesis of SBA-15. Pluronic® P123 (8.0 g, $M_w = 5800$, Aldrich), deionized (DI) water (251.4 g), and 35% HCl (48.6 g, 35 wt%, Samchun) were added to a 500 mL polypropylene bottle, and the resulting mixture was stirred at 35 °C for 1 h. After the P123 was completely dissolved, tetraethyl orthosilicate (17.0 g, 98%, Aldrich) was added and the solution was stirred for 5 min and aged at 35 °C without stirring for 24 h. The reaction mixture was transferred into a Teflon®-lined autoclave and heated at 150 °C for 24 h. The resulting precipitate was filtered, washed twice with DI water, and then dried in an oven at 60 °C for 1 d. The dried sample was calcined at 550 °C for 5 h in air.

Synthesis of OMC. A solution containing the aromatic mesophase pitch (3.02 g, Mitsubishi Gas Chemical Company) and tetrahydrofuran (80 mL, OCI) was sonicated for 1 h. SBA-15 (2.0 g) was added to the solution, and the resulting mixture was stirred at room temperature for 1 h and then dried in an oven at 60 °C overnight. The dried mixture was added to a quartz tube furnace and heated to 350 °C at a rate of 1.4 °C min⁻¹, which exceeds the softening point of the aromatic mesophase pitch (320 °C). After maintaining the mixture at 350 °C for 4 h, it was heated to 900 °C at a rate of 2.6 °C min⁻¹ and kept at this temperature for 2 h. The resulting carbon–silica composite was then washed twice with 10 wt% hydrofluoric acid (J.T. Baker) at room temperature for 1 h to remove the SBA-15 template.^{S1-S2}

Synthesis of O-OMC. Sucrose (1.375 g, Samchun) and 95% H₂SO₄ (0.14 g, Samchun) were dissolved in DI water (5 g). SBA-15 (1 g) was added to the solution and the resulting mixture placed in an oven at 100 °C for 6 h. The oven temperature was increased to 160 °C and kept at 160 °C for 6 h. The silica–carbon composite was added to a solution containing sucrose (0.83 g), H₂SO₄ (0.09 g), and DI water (5 g). The reaction mixture was heated at 100 °C for 6 h and increased to 160 °C for a further 6 h. The carbonization was carried out by pyrolysis upon heating to 900 °C under a flow of nitrogen for 2 h. The silica was leached out using the same procedure as described for OMC.^{S3}

Synthesis of N,O-OMC. SBA-15 (1 g) was added to a solution of glucosamine (1.54 g, Aldrich), H₂SO₄ (0.17 g), and DI water (5 g). The mixture was placed in an oven and treated at 100 °C and 160 °C using the same procedure described for O-OMC. The composite was added to a solution

containing glucosamine (0.96 g), H₂SO₄ (0.11 g), and DI water (5 g) and heated at 100 °C and 160 °C as described for O-OMC. The mixture was then heated to 900 °C at a ramping rate of 2.5 °C min⁻¹, and kept at this temperature for 3 h under a flow of nitrogen. The silica was leached out using the same procedure as described for the OMC.

Synthesis of S,O-OMC. SBA-15 (1 g) was added to a solution of *p*-toluenesulfonic acid (1.85 g, Aldrich) and acetone (1.85 g, Samchun). The composite material was placed in an oven and heated at 100 °C and 160 °C using the same procedure described for O-OMC. The infiltration-drying process was repeated using a solution containing *p*-toluenesulfonic acid (1.85 g) and acetone (1.15 g). The resulting mixture was carbonized at 900 °C under a flow of nitrogen for 3 h. S,O-OMC was obtained upon leaching the silica using the same procedure as described for the OMC.^{S4}

Synthesis of N,S,O-OMC. SBA-15 (1 g) was added to a solution containing glucosamine (0.76 g), *p*-toluenesulfonic acid (0.92 g), H₂SO₄ (0.08 g), and DI water (5 g). The mixture was heated at 100 °C and 160 °C using the same procedure described for O-OMC. The infiltration-drying process was repeated using 66 w/w% of the initial reactants with the exception of DI water (5 g). The N,S,O-OMC was obtained after carbonization and acid washing using the procedure as described for the OMC.

Characterization methods. All characterization was carried out at the Ulsan National Institute of Science and Technology (UNIST) Central Research Facilities (UCRF) Center. X-ray photoelectron spectroscopy (XPS) was performed using a K-alpha instrument from Thermo Fisher. X-ray powder diffraction (XRPD) data was measured using a Rigaku D/MAZX 2500V/PC diffractometer at 40 kV and 200 mA equipped with a Cu K α (λ = 1.5418 Å) source, with a step size of 0.02° in 2θ . Transmission electron microscopy (TEM) images were obtained using a JEOL JEM-2100 microscope. High-angle annular dark-field scanning transmission electron microscopy (HAADF STEM) images and the corresponding elemental mapping images were obtained using a JEOL JEM-2100F microscope. The morphologies of the samples were observed using a Hitachi S-4800 scanning electron microscope (SEM) operating at 10 kV. The nitrogen adsorption-desorption isotherms were measured at -196 °C using liquid nitrogen on a BELSORP-MAX instrument. Prior to the adsorption measurement, the samples were evacuated at 200 °C under vacuum ($p < 10^{-5}$ mbar) for 12 h. The specific surface area was determined in

the relative pressure range of 0.05 - 0.3 of the Brunauer–Emmett–Teller (BET) plot and the total pore volume calculated from the amount adsorbed at a relative pressure of ~ 0.98 – 0.99 . The pore size distribution was obtained using the Barrett–Joyner–Halenda (BJH) method. This data is summarized in Table S1.

Electrochemical Characterization. Electrochemical characterization of the samples was carried out using an IviumStat electrochemical analyzer. The electrochemical experiments were performed at room temperature ($25\text{ }^{\circ}\text{C}$) under atmospheric pressure using a three-compartment electrochemical cell. A graphite counter electrode and Hg/HgO reference electrode (XR400, Radiometer Analytical) with 1 M KOH (99.999%, Aldrich) filling solution were used. The Hg/HgO reference electrode was calibrated to the reversible hydrogen electrode (RHE) before every measurement.

For the ORR performance measurement, a rotating ring disk electrode (RRDE) with a glassy carbon disk (GC, 4 mm in diameter) and a Pt ring (5 mm in inner diameter and 7 mm in outer diameter) was used as the working electrode (ALS, Cat. No. 012613). The RRDE was polished with 1.0 and 0.3 μm alumina suspensions to generate a mirror finish. The catalyst ink was prepared by mixing the catalyst (7.5 mg), Nafion (75 μL), deionized water (100 μL), and ethanol (1.01 mL, >99.9%, Samchun) [for Pt/C catalyst, 5 mg of 20 wt% Pt/C (Johnson & Matthey, HiSPEC 3000), 40 μL of Nafion, and 1.15 mL of ethanol were used] using ultrasonication for at least 30 min. The resulting catalyst loading was 0.15 mg cm^{-2} , except Pt/C catalyst ($0.1\text{ mg}_{\text{cat}}\text{ cm}^{-2}$). Prior to the electrochemical measurements, a potential cycle from 0.05 to 1.2 V was applied in a N_2 -saturated solution of 0.1 M KOH for 50 cycles at a scan rate of 100 mV s^{-1} for electrochemical cleaning. The cyclic voltammogram was obtained under the same conditions used for electrochemical cleaning, except the scan rate was changed to 20 mV s^{-1} for 3 cycles. Linear sweep voltammetry (LSV) curves for the ORR were obtained using a potential cycle from 1.1 to 0.2 V (for Pt/C, LSV curve was obtained from 0.2 to 1.1 to avoid the formation of Pt-O species.) in an O_2 -saturated solution of 0.1 M KOH with O_2 purging at different rotating speeds. The ORR measurement was independently repeated three times, and the averaged currents were used.

For the evaluation of four-electron selectivity, the potential of the Pt ring was fixed at 1.3 V (vs. RHE) during LSV scans for the ORR. The number of electrons transferred was calculated by

$$n = \frac{4}{1 + \frac{I_R}{N \times I_D}}$$

where: I_D , I_R , and N are the disk current, the ring current, and the collection coefficient, respectively. The value of N was determined to be 0.44 in a 1 M KNO_3 + 2 mM $\text{K}_3\text{Fe}(\text{CN})_6$ solution at a rotating speed of 1000 rpm.

The ORR activity and four-electron selectivity of the undoped/doped OMC catalysts were also evaluated in acid using the same experimental conditions, except the use of 0.1 M HClO_4 electrolyte.

Transfer of the OMCs onto gold-coated Si-substrates. It was essential to separate the OMC nanostructure and still have the individual nanostructures connected to the substrate for accurate CPD measurements. A drop-casting method was used in a two-step process. Undoped/doped OMC nanostructures (10 mg) were mixed with a solution of ethanol (2 mg) in water (10 mg) followed by 30 min of sonication for separation. A 2 ml portion of the solution was transferred into a vial and ethanol (5 ml) was added. After sonication for 1 h, several drops of the solution were transferred onto the substrate using a syringe. After the solvent evaporated, the SEM measurement was carried out to confirm the distribution and elucidate the ideal position for KPFM (Figure S19).

KPFM measurement. KPFM is a quantitative method to evaluate changes in the electrostatic field or work function on the surface. The electrostatic force (F_e) between the tip and the sample can be described by the following equation:

$$F_e(z) = -\frac{dC}{dz}\Delta V^2$$

where: z and C are the distance and capacitance between the tip and sample, respectively. Provided with an AC voltage ($V_{ac} \sin \omega t$) and a DC voltage (V_{dc}) to a conductive tip, the voltage difference (ΔV) becomes $V_{dc} + V_{ac} \sin \omega t - V_{cpd}$. The equation can be divided into terms of frequency:

$$F_{dc}(z) = -\frac{1}{2}\frac{dC}{dz}(V_{dc} - V_{cpd})^2$$

$$F_{1\omega}(z) = -\frac{1}{2} \frac{dC}{dz} (V_{dc} - V_{cpd}) V_{ac} \sin \omega t$$

$$F_{2\omega}(z) = \frac{1}{4} \frac{dC}{dz} (\cos 2\omega t - 1) V_{ac}^2$$

Thus, if the 1ω signal is extracted from the AFM oscillation signal using the lock-in technique and a feedback system is employed to provide a signal to nullify the value, V_{cpd} can be obtained.

In our KPFM experiment, we utilized an Agilent 5500 AFM with a conductive non-contact cantilever coated with Pt/Ir. The nominal resonance frequency (f_0) which was utilized in mapping topography, was ~ 75 kHz. Additionally, a 1 V sinusoidal signal with the frequency of 10 kHz was applied for the CPD measurement.

References for Supporting Information

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Table S1. BET surface areas, pore volumes, and pore sizes of the doped OMCs.

Sample	BET surface area ^a (m ² g ⁻¹)	Pore volume ^b (cm ³ g ⁻¹)	Pore size ^c (nm)
O-OMC	1550	1.48	5.5
N,O-OMC	534	1.08	5.5
S,O-OMC	1080	1.22	5.5
N,S,O-OMC	1060	1.85	9.3

^a BET surface area was calculated in the relative pressure range of 0.05–0.3.

^b Pore volume was calculated at the relative pressure of 0.98–0.99.

^c Pore size was calculated by the BJH method using the adsorption branches of isotherms.

Table S2. Chemical compositions of the undoped and doped OMCs (at%).^a

Sample	C	N	S	O
OMC	97.8	-	-	2.2
O-OMC	93.5	-	-	6.4
N,O-OMC	85.9	2.4	-	11.6
S,O-OMC	91.7	-	3.5	4.8
N,S,O-OMC	90.3	2.1	0.7	6.9

^a Chemical compositions of the doped OMCs were obtained from XPS analysis.

Table S3. ORR activity and reaction kinetics of the undoped and doped OMCs

Sample	On-set potential (V vs RHE)	Half-wave potential (V vs RHE)	Kinetic current at 0.75 V vs RHE (mA cm ⁻²)	Electron transfer number at 0.6 V vs RHE
OMC	0.77	0.69	0.3	2.2
O-OMC	0.80	0.71	1.2	2.5
N,O-OMC	0.84	0.74	2.5	3.2
S,O-OMC	0.79	0.70	0.5	2.7
N,S,O-OMC	0.85	0.75	3.8	3.5

Figure S1. (a) SEM and (b) TEM images of the SBA-15 mesoporous silica template.

Figure S2. SEM images of the doped OMCs: (a) O-OMC, (b) N,O-OMC, (c) S,O-OMC, and (d) N,S,O-OMC.

Figure S3. TEM images of the doped OMCs: (a) O-OMC, (b) N,O-OMC, (c) S,O-OMC, and (d) N,S,O-OMC.

Figure S4. (a) Small-angle and (b) wide-angle XRD patterns of the doped OMCs.

Figure S5. (a) N₂ adsorption-desorption isotherms of the doped OMCs and (b) their corresponding pore size distribution curves obtained from the adsorption branches.

Figure S6. (a) HAADF STEM image of the N,S,O-OMC and the corresponding elemental mapping images of (b) carbon, (c) nitrogen, (d) sulfur, and (e) oxygen.

Figure S7. (a) HAADF STEM image of the O-OMC and the corresponding elemental mapping images of (b) carbon and (c) oxygen.

Figure S8. (a) HAADF STEM image of the N,O-OMC and the corresponding elemental mapping images of (b) carbon, (c) nitrogen, and (d) oxygen.

Figure S9. (a) HAADF STEM image of the S,O-OMC and the corresponding elemental mapping images of (b) carbon, (c) sulfur, and (d) oxygen.

Figure S10. XPS spectra of the N,S,O-OMC: (a) survey scan, (b) N 1s, (c) S 2p, and (d) O 1s spectra.

Figure S11. XPS spectra of the O-OMC: (a) survey scan, (b) C 1s, and (c) O 1s spectra.

Figure S12. XPS spectra of the N,O-OMC: (a) survey scan, (b) C 1s, (c) N 1s, and (d) O 1s spectra.

Figure S13. XPS spectra of the S,O-OMC: (a) survey scan, (b) C 1s, (c) S 2p, and (d) O 1s spectra.

Figure S14. Comparison of XPS spectra of the OMC (bottom) and the O-OMC (top): (a) C 1s and (b) O 1s spectra.

Figure S15. RRDE voltammograms of the undoped and doped OMCs in oxygen-saturated solution of 0.1M KOH at different rotating speeds and scan rate of 5 mV s^{-1} : (a) OMC, (b) O-OMC, (c) N,O-OMC, (d) S,O-OMC, and (e) N,S,O-OMC.

Figure S16. Tafel plots for the undoped and doped OMC catalysts.

Figure S17. LSV curves of the undoped and doped OMCs and Pt/C catalyst for the ORR.

Figure S18. H₂O₂ yields of the undoped and doped OMCs calculated from the measurement of the ring current during the ORR.

Figure S19. SEM images of the undoped and doped OMCs transferred onto an Au-coated Si substrate: (a) OMC, (b) O-OMC, (c) S,O-OMC, (d) N,O-OMC, and (e) N,S,O-OMC.

Figure S20. Topography images of the undoped and doped OMCs (top) and their CPD maps (bottom) corresponding to the insets in Figure 4a. Scale bar is 200 nm.

Figure S21. (a) LSV curves of the undoped and doped OMCs for the ORR in 0.1 M HClO₄. (b,c) Corresponding correlation of the ORR activity (b) and four-electron selectivity (c) with their work function values.