Electronic Supplementary Information (ESI)

Organic Precursors for Tailored Synthesis of Sulfur- and Nitrogen-Doped Mesoporous Carbons: A Molecular Design Approach

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Experimental

Materials

Methyltriphenylphosphonium bromide, 3,4-dimethoxybenzaldehyde, thioacetic acid, and 1,3,5-trimethylbenzene were obtained from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan) and used without further purification. Poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) (PEO-PPO-PEO) (F-127) with a molecular weight of 12,600 was purchased from Sigma-Aldrich. A 1.6 M solution of n-butyllithium (n-BuLi) in n-hexane was acquired from Kanto Chemical Co., Ltd and used as received. A 1 mol/L solution of boron tribromide in dichloromethane, 2,2′-azobis(isobutyronitrile) (AIBN), dichloromethane, ethyl acetate, hexane, tetrahydrofuran (THF), toluene, sodium hydroxide (NaOH), hydrochloric acid (HCl) were purchased from FUJIFILM Wako Pure Chemical Co., Ltd (Osaka, Japan). AIBN was purified by recrystallization from methanol. Dichloromethane, THF, and toluene were distilled over calcium hydride. All other chemicals were used as received.


Measurements

^{1}H and ^{13}C nuclear magnetic resonance (NMR) measurements were conducted on a Bruker 300 MHz NMR spectrometer in deuterated chloroform (CDCl$_3$) or deuterated tetrahydrofuran (d_8-THF), using residual chloroform or THF as a reference. High resolution mass spectrometry (HRMS) was measured by a JEOL JMS-T100GCV (EI) spectrometer. Thermogravimetric analysis (TGA) was conducted on Rigaku TG-DTA8122 at a heating rate of 5 °C/min under a nitrogen flow of 100 mL/min. Scanning electron microscopy (SEM) was carried

out using a ZEISS GeminiSEM 560 equipped with energy-dispersive X-ray spectroscopy (EDX). Scanning transmission electron microscope (STEM) and high-resolution TEM (HRTEM) were conducted by using an HF5000 (Hitachi) at 200 kV. Small-angle X-ray scattering (SAXS) experiments were performed using a Rigaku Nanoviewer X-ray diffractometer. Nitrogen adsorption measurements were conducted using an Anton Paar QuantaTec Autosorb IQ. The samples were degassed under vacuum at 100 °C for 24 h before measurements. The surface areas were estimated using the Multipoint Brunauer-Emmett-Teller (BET) method at a P/P0 range of 0.05-1.0 based on the adsorption data. The total pore volumes and pore size distributions were calculated from the adsorption branches of isotherms based on density functional theory (DFT). X-ray photoelectron spectroscopy (XPS) was measured by Thermal VG ESCALAB250.

Synthesis of sulfur-containing monomer

Sulfur-containing monomer was synthesized in a four-step reaction following previous papers.[1,2] 3,4-Dimethoxystyrene was synthesized via Wittig reaction in 88% yield. Thioacetyl group was introduced through thiol-ene reaction to afford [2-(3,4-dimethoxyphenyl)ethyl]thioacetate in 82% yield. The deprotection of methoxy group with boron tribromide gave 82% yield of [2-(3,4-dihydroxyphenyl)ethyl]thioacetate. Thiol-ene reaction and deprotection proceeded quantitatively. 1,2-Dihydroxy-4-(2-mercaptoethyl)benzene was synthesized in 57% yield by hydrolysis. Sulfur-containing monomer was obtained as a white solid, total yield 34%. The detailed synthetic procedure is as follows:

## Synthesis of 3,4-dimethoxystyrene
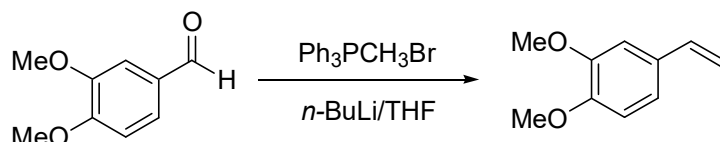
In a dry 100 mL Schlenk flask, methyltriphenylphosphonium bromide (9.99 g, 28.0 mmol) was suspended in 50 mL of THF. A solution of 15.1 mL of n-BuLi (1.60 mol/L in hexane) was slowly added to this suspension at 0 °C, and the mixture was stirred at room temperature for 1 h under a nitrogen atmosphere. Subsequently, 3,4-dimethoxybenzaldehyde (3.32 g, 20 mmol) in 20 mL of THF was added dropwise via syringe, and the reaction mixture was stirred at room temperature overnight under a nitrogen atmosphere. THF was evaporated under reduced pressure, and the residue was dissolved in dichloromethane and washed with water three times. The organic layer was dried over sodium sulfate, and the dichloromethane solution was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel eluting with ethyl acetate–hexane (1:4) to afford 3,4-dimethoxystyrene as a colorless liquid (2.88 g, 88% yield).

^{1}H NMR (300 MHz, CDCl$_3$): 6.95 (2H, m), 6.81 (1H, d, J = 6.8), 6.65 (1H, dd, J = 14, 8.8 Hz), 5.61 (1H, d, J = 14 Hz), 5.14 (1H, d, J = 8.8 Hz), 3.89 (3H, s), 3.87 (3H, s).

^{13}C NMR (75 MHz, CDCl$_3$): 55.8, 55.9, 108.5, 111.0, 111.8, 119.5, 130,7, 136.5, 148.9, 149.0.

HRMS (EI, positive): calcd for $C_{10}H_{12}O_2$ m/z = 164.08373 [M$^+$], found m/z = 164.08385.

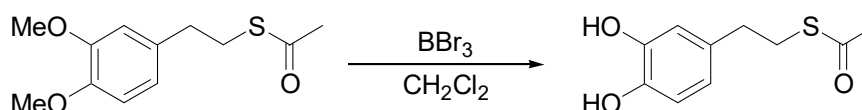**Synthesis of [2-(3,4-dimethoxyphenyl)ethyl]thioacetate**
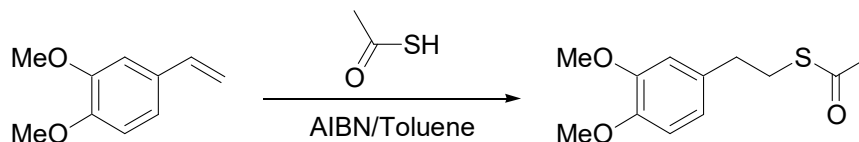
In a dry 50 mL Schlenk flask, 3,4-dimethoxystyrene (8.00 g, 48.7 mmol), thioacetic acid (4.16 mL, 58.5 mmol), and AIBN (192 mg, 1.17 mmol) were dissolved in 80 mL of toluene. The resulting solution was heated at 80 °C for 6 h under a nitrogen atmosphere. After cooling to room temperature, toluene was evaporated under reduced pressure, and the residue was purified by column chromatography on silica gel eluting with ethyl acetate–hexane (1:4) to afford [2-(3,4-dimethoxyphenyl)ethyl]thioacetate as a white solid (9.55 g, 82% yield).

^{1}H NMR (300 MHz, CDCl$_3$): 6.79 (3H, m), 3.89 (3H, s), 3.86 (3H, s), 3.11 (2H, t, J = 7.7), 2.82 (2H, t, J = 7.7), 2.34 (3H, s).

^{13}C NMR (75 MHz, CDCl$_3$): 30.6, 30.7, 35.4, 55.8, 55.9, 111.2, 111.7, 120.5, 132.6, 147.7, 148.9. 195.8.

HRMS (EI, positive): calcd for $C_{12}H_{16}O_3S$ m/z = 240.08201 [M$^+$], found m/z = 240.08244.

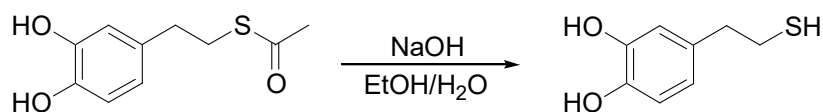**Synthesis of [2-(3,4-dihydroxyphenyl)ethyl]thioacetate**

In a dry 200 mL two-necked flask, [2-(3,4-dimethoxyphenyl)ethyl]thioacetate (5.09 g, 21.2 mmol) was dissolved in 70 mL of dichloromethane, and the solution was cooled to −78 °C (dry ice/acetone) under a nitrogen atmosphere. A solution of boron tribromide (46.6 mL, 46.6 mmol) was slowly added dropwise. Then, the resulting solution was refluxed for 5 h and subsequently stirred at room temperature overnight. Thirty milliliters of water was slowly added to quench excess boron tribromide, and the organic layer was separated. The aqueous layer was extracted with dichloromethane three times. The combined organic layer was dried over magnesium sulfate, and the dichloromethane solution was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel eluting with ethyl acetate–hexane (1:2) to afford [2-(3,4-dihydroxyphenyl)ethyl]thioacetate as a white solid (4.20 g, 82% yield).

^{1}H NMR (300 MHz, CDCl$_3$): 6.75 (2H, m), 6.58 (1H, m), 6.21 (2H, brd), 3.03 (2H, t, J = 7.7 Hz), 2.70 (2H, t, J = 7.7 Hz), 2.31 (3H, s).

^{13}C NMR (75 MHz, CDCl$_3$): 30.7, 30.8, 35.0, 115.4, 115.7, 120.9, 132.7, 142.4, 143.7, 197.9.

HRMS (EI, positive): calcd for $C_{10}H_{12}O_3S$ m/z = 212.05071 [M$^+$], found m/z = 212.05089.

Synthesis of 1,2-dihydroxy-4-(2-mercaptoethyl)benzene

In a 50 mL two-necked flask, [2-(3,4-dihydroxyphenyl)ethyl]thioacetate (3.90 g, 18.4 mmol) was dissolved in a mixture of 0.2 mol/L NaOH solution (37 mL) and ethanol (37 mL). The resulting solution was stirred at room temperature overnight. Then, 37 mL of 0.2 mol/L HCl solution was added for neutralization, and the resulting mixture was extracted with ethyl acetate five times. The combined organic layer was dried over magnesium sulfate, and the ethyl acetate was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel eluting with ethyl acetate–hexane (1:2) to afford 1,2-dihydroxy-4-(2-mercaptoethyl)benzene as a white solid (2.54 g, 57% yield).

^{1}H NMR (300 MHz, d_8-THF): 7.76 (2H, s), 6.59 (2H, m), 6.45 (1H, dd, J = 2.1, 8.2), 2.68 (4H, m), 1.58 (1H, t, J = 7.7).

^{13}C NMR (75 MHz, d_8-THF): 26.7, 40.8, 115.6, 116.1, 120.0, 132,2, 144,7, 146,1.

HRMS (EI, positive): calcd for $C_8H_{10}O_2S$ m/z = 170.04015 [M$^+$], found m/z = 170.04075.

Preparation of nitrogen-doped polymer aggregate

Nitrogen-doped polymer aggregate was prepared according to a previously reported procedure.[3] In a 50 mL vial, 100 mg of F-127 was dissolved in a mixture of deionized water (9 mL) and ethanol (9 mL) using sonication, and the solution was stirred at room temperature for 5 min. Subsequently, 200 μL of trimethylbenzene was added and stirred at room temperature. After 5 min, 100 mg of dopamine dissolved in a mixture of deionized water (1 mL) and ethanol (1 mL) was added and stirred at room temperature for 5 min. Finally, 200 μL of ammonia solution (28% in water) was added and stirred at room temperature. After 3 days, the black solid was obtained by centrifugation at 15,000 rpm for 15 min. The black solid was dispersed in a mixture of deionized water (10 mL) and ethanol (10 mL) and centrifuged under the same conditions two times. Finally, the black solid was dispersed in 20 mL of ethanol and centrifuged under the same conditions. The black solid was obtained with a yield of 21.7 mg after drying in a vacuum desiccator for several hours. Sulfur-doped polymer aggregate was also prepared by the same way, except for the use of sulfur-containing monomer.

Preparation of nitrogen-doped mesoporous carbon (NMC)

For carbonization, nitrogen-doped polymer aggregates were heated from room temperature to 900 °C at a heating rate of 5 °C/min under a nitrogen flow of 100 mL/min and maintained at this temperature for 2 h. The black solid was obtained after cooling down to room temperature. Sulfur-doped mesoporous carbon (SMC) was also prepared by the same way.

Electrochemical measurements

To prepare an ink, 5.0 mg of the NMC was ground, followed by dispersing in a 950 μL mixture of deionized water and isopropanol (2:1 vol, v/v) and 50 μL of a 5 wt.% Nafion solution. The suspension was ultrasonicated for at least 60 minutes to obtain a homogeneous ink (catalyst concentration of 5 mg/mL). A 10 μL aliquot of the ink was drop-cast on a glassy carbon disk electrode with a diameter of 4 mm, along with a Pt ring electrode, to obtain a working electrode with a catalyst density of 0.40 mg/cm^2.

The oxygen reduction reaction (ORR) measurements were carried out in a typical three-electrode system in an aqueous 0.1 M KOH electrolyte. An Hg/HgO (1 M NaOH) electrode (0.903 V vs RHE) and a carbon rod were used as the reference electrode and counter electrode, respectively. Linear sweep voltammetry was conducted with a scan rate of 10 mV/s and a rotating speed of 1600 rpm. Before the ORR measurements, the working electrode was electrochemically polished by cyclic voltammetry with a scan rate of 100 mV/s, scanning between 0.01 and 1.15 V vs. RHE for 250 cycles.
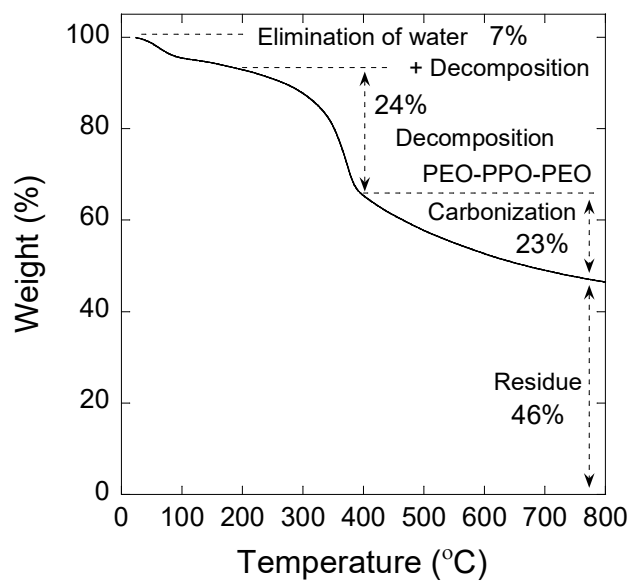
Fig. S1 The TGA trace of the carbonization of aggregates prepared from the dopamine for the preparation of NMC.
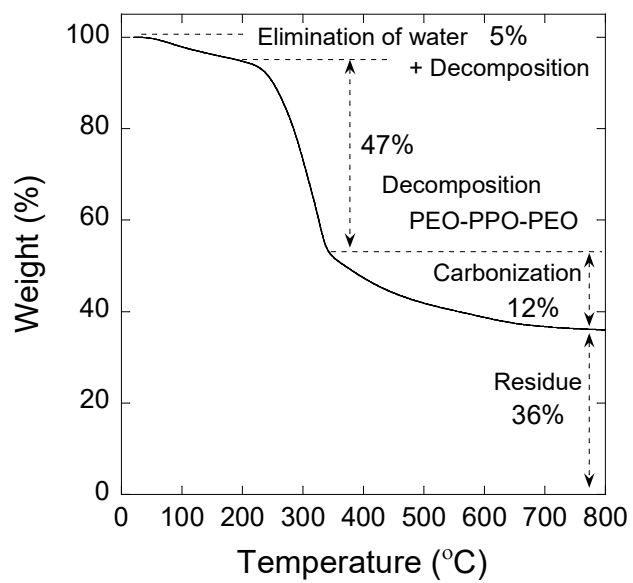
Fig. S2 The TGA trace of the carbonization of aggregates prepared from the sulfur-containing monomer for the preparation of SMC.
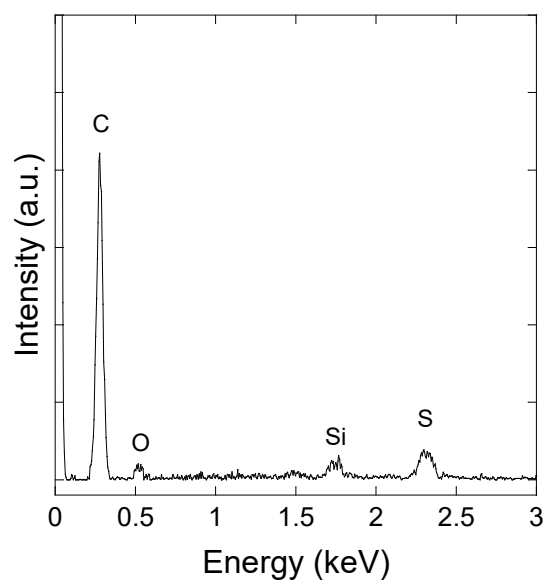
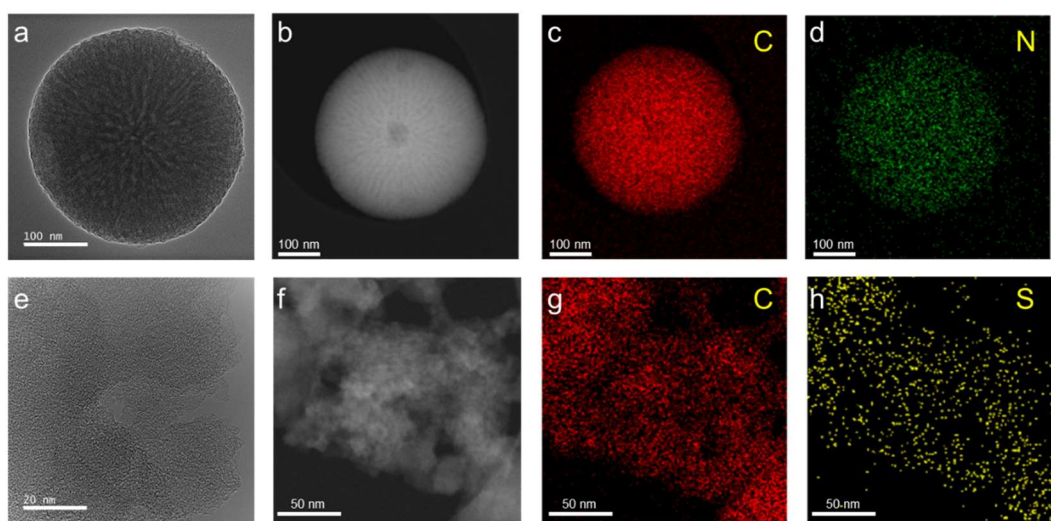**Fig. S3** SEM-EDX spectrum of SMC obtained through carbonization at 900 °C for 2 hours.

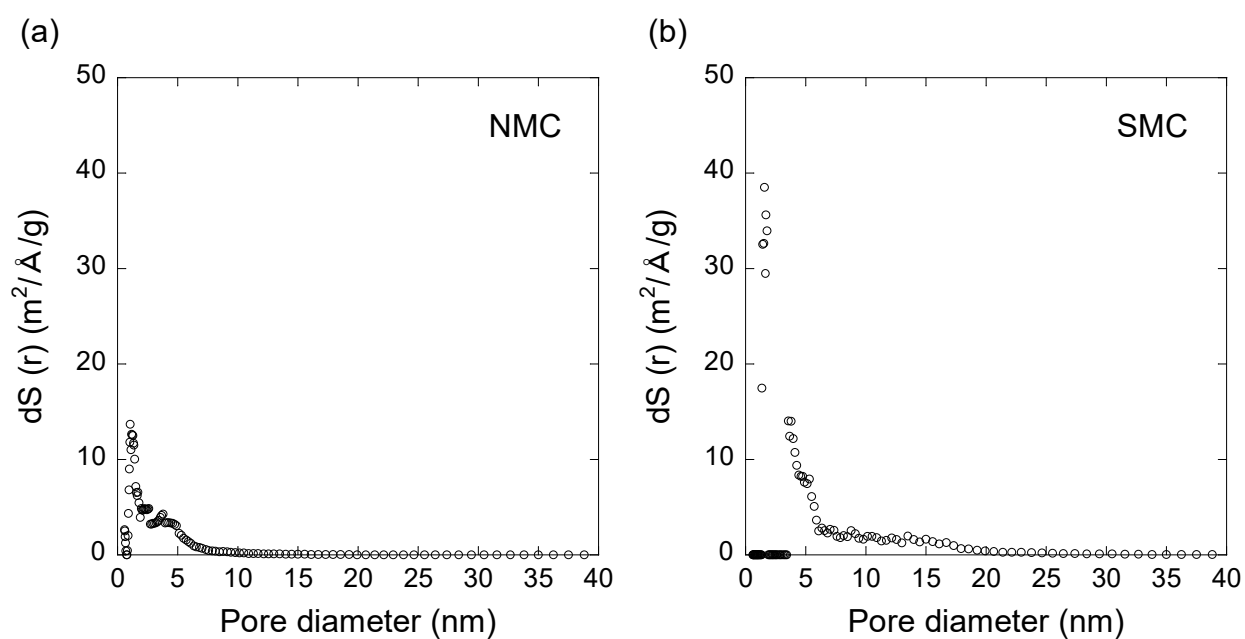**Fig. S4** HRTEM images of (a and b) NMC and (e and f) SMC, along with STEM-EDX element mappings of (c and d) NMC and (g and h) SMC.

Fig. S5 Mesopore size distribution in (a) NMC and (b) SMC calculated from nitrogen adsorption isotherms using density functional theory (DFT).
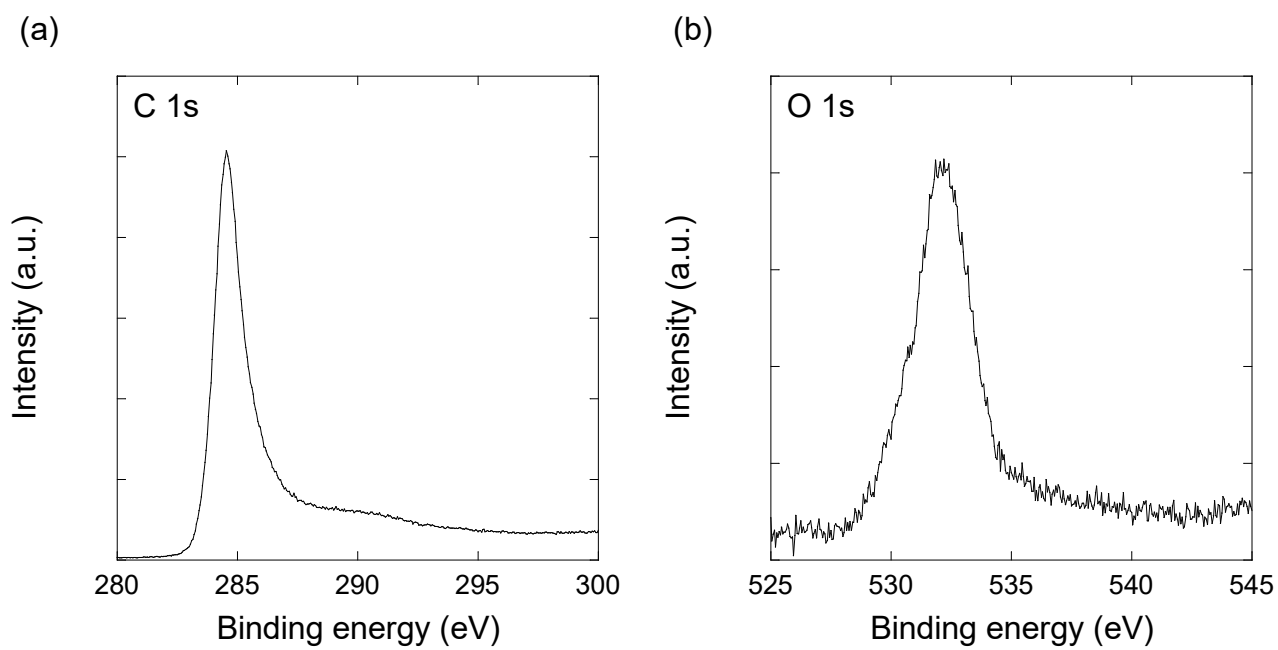
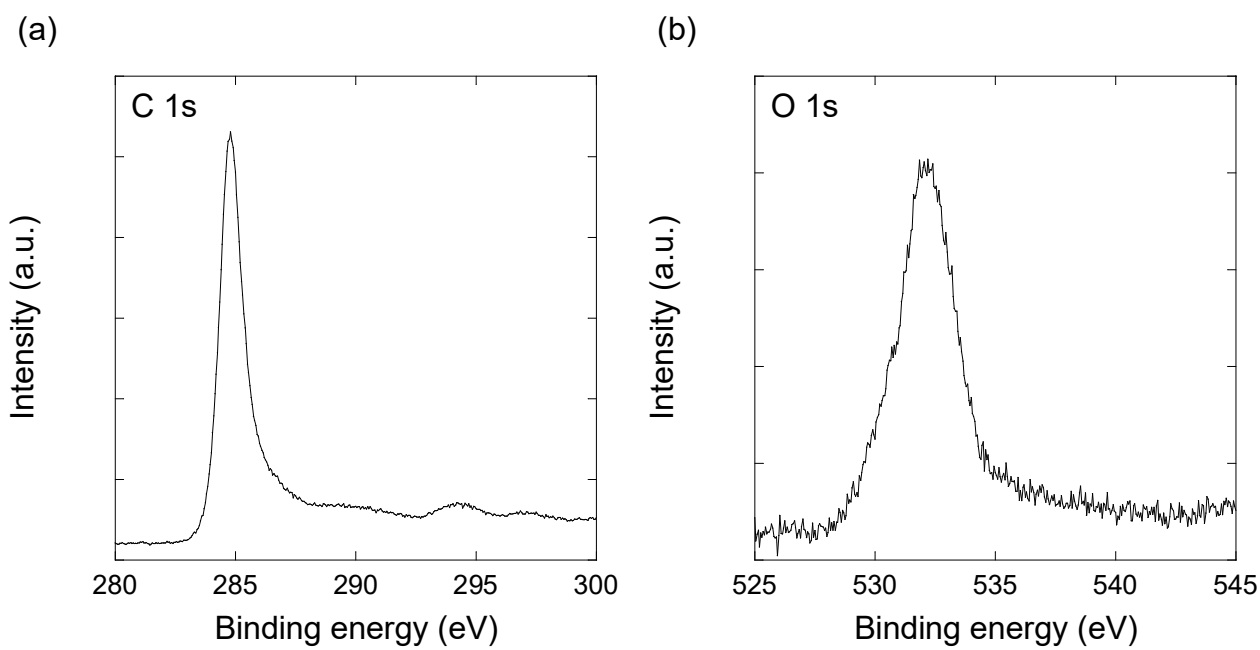**Fig. S6** XPS spectra of (a) C 1s and (b) O 1s for NMC.

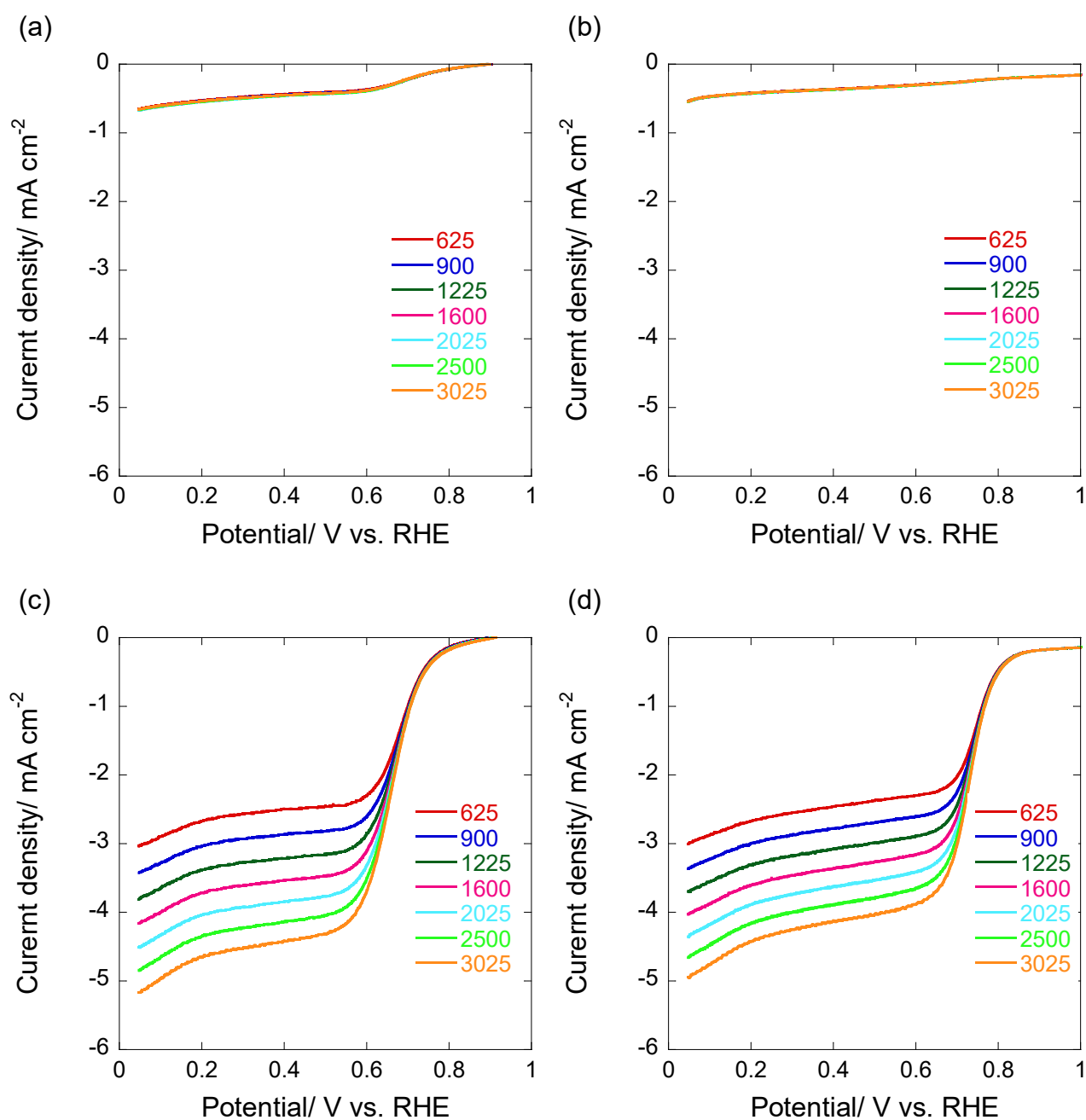**Fig. S7** XPS spectra of (a) C 1s and (b) O 1s for SMC.

Fig. S8 LSV with various rotation speed of (a) and (b) in N_2-saturated 0.1 M KOH, and (c) and (d) in O_2-saturated 0.1 M KOH of NMC and SMC, respectively.
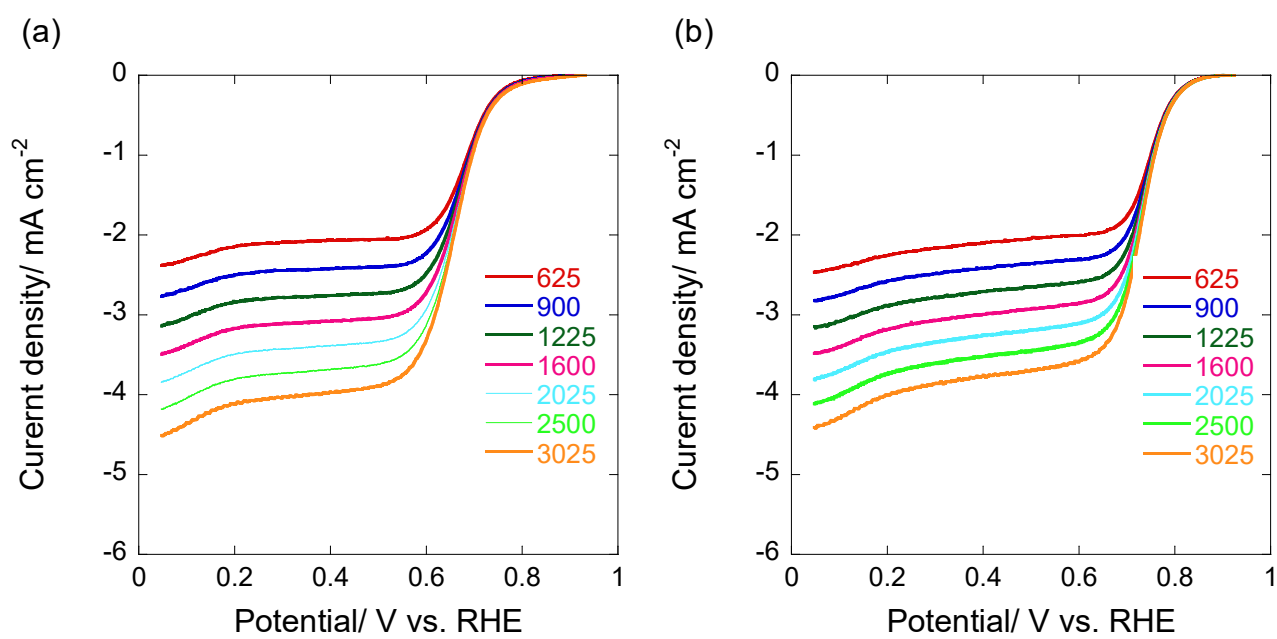
Fig. S9 Background-substituted LSV with various rotation speed of (a) NMC and (b) SMC, respectively.
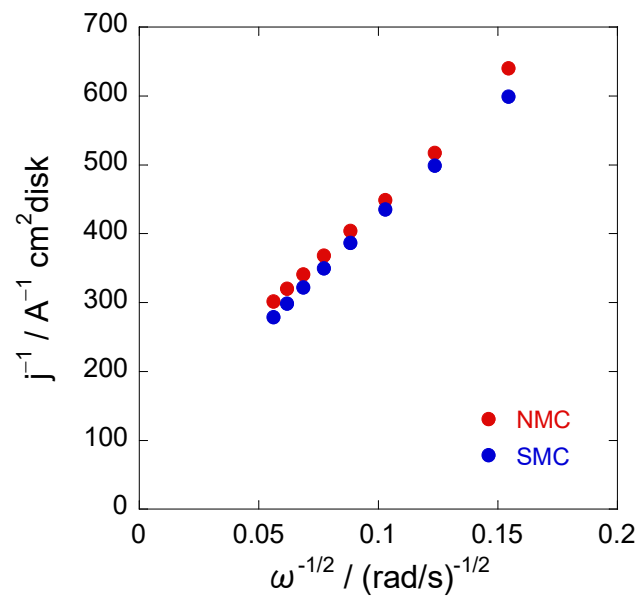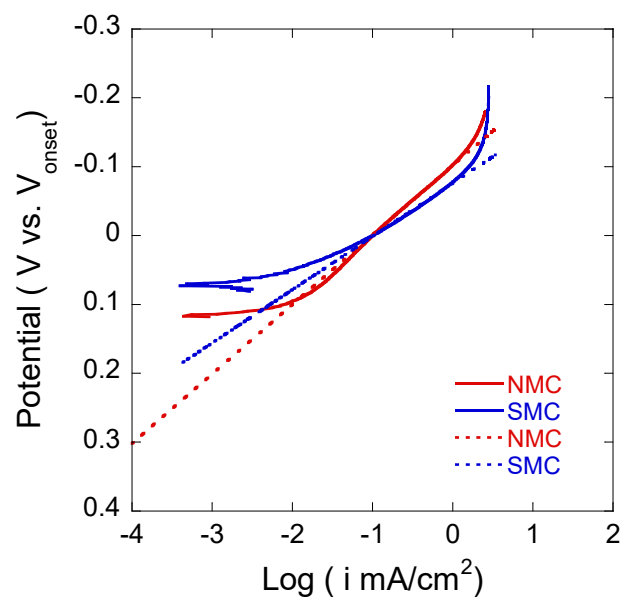
Fig. S10 K-L plots of NMC and SMC, respectively.

Fig. S11 Tafel plots of NMC and SMC, respectively.

Table S1. Catalytic activity of NMC and SMC

	E_{onset} (V vs RHE)	$E_{1/2}$ (V vs RHE)	Tafel slope (mV/decade)
NMC	0.796	0.667	101
SMC	0.833	0.733	77

References

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