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Electronic Supplementary Information (ESI)

Efficiency and long-term durability of a nitrogen-doped single-walled carbon nanotube electrocatalyst synthesized by defluorination-assisted nanotube-substitution for oxygen reduction reaction

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Contents

Materials and Methods

Preparation of hc-SWCNTs

We synthesized SWCNTs by the arc discharge method using a mixture of Fe/Ni particles as the metal catalyst. To remove any amorphous carbon, 1.0 g of the as-formed soot was oxidized in air at 450 °C for 30 min. The resulting soot was then oxidized again in air at 500 °C for 30 min by continuous air oxidization. Next, the oxidized soot was introduced into a flask containing a 6.0 mol/L aqueous hydrochloric acid (Special Grade, Wako Pure Chemicals, Co., Japan) solution, in order to dissolve the metal particles. The resultant suspension was filtered using a polytetrafluoroethylene (PTFE) membrane filter with an average pore diameter of 0.1 μm (ADVANTEC, Japan), and the filtered cake was washed with purified water. The resulting sample was dried in air at 60 °C for 12 h. Following this procedure, the dried material was again oxidized in air at 500 °C for 30 min to remove the remaining thin graphene capsules covering catalytic metal particles and treated with a 6.0 mol/L aqueous hydrochloric acid solution in an effort to remove the remaining catalytic metal particles. Finally, the resulting suspension was filtered using a PTFE membrane filter with an average pore diameter of 0.1 μm, and the filtered cake was washed with purified water. The resulting sample was dried in air at 60 °C for 12 h and then dried in vacuum at 200 °C for 24 h. Next, the purified SWCNTs were annealed in high vacuum to remove the attached functional groups and restore the hexagonal graphene network. 150 mg of the resultant sample was put into a graphite crucible, which was placed on a graphite plate around a C/C composite heater. After the chamber had been evacuated, the sample was heated under high vacuum (1.0×10^{-5} Pa) at 1200 °C for 3 h.[S1-S3]

Synthesis of $F_{2.69at\%}$-SWCNTs

50 mg of the hc-SWCNTs were put in a polytetrafluoroethylene (PTFE) tube (inner diameter of 6.0 mm). The PTFE tube was then placed at the center of a stainless steel tube (inner diameter of 10 mm), which was kept at the center of a tubular electric furnace. After the hc-SWCNTs had been annealed in vacuum at 250 °C for 2 h in order to remove the water adsorbed on them, they were fluorinated at 25 °C using a gas mixture of 20% F_2/N_2 for 1 h (flow rate of 25 mL/min). Subsequently, they were subjected to thermal annealing at 25 °C for 1 h in a nitrogen flow (20 mL/min). The fluorinated SWCNTs were characterized using XPS (Fig. S2). From the XPS data, their C:F stoichiometry was determined to be $CF_{0.03}$ (see Table S2).

Synthesis of $F_{5.62at\%}$-SWCNTs

$F_{5.62at\%}$-SWCNTs were synthesized by the same method as the synthesis of the $F_{2.69at\%}$-SWCNTs except a reaction time of 4 h. From the XPS data, their C:F stoichiometry was determined to be $CF_{0.06}$ (see Table S2).

CV and LSV measurement procedures

Each CV measurement was carried out as follows. After the catalytic electrode had undergone five cleaning cycles in O_2-saturated electrolyte (scan rate: 50 mV s^{-1}, potential range: -0.5 to +1.0 V), a CV curve was recorded at the scan rate of 10 mV s^{-1}. Then the same operation was repeated in the N_2-saturated electrolyte. Each LSV measurement was first carried out in N_2-saturated electrolyte to obtain the background curve (scan rate: 10 mV s^{-1}, potential range: -0.3 to +0.8 V). Then the curves in O_2-saturated electrolyte at rotation rates of 400–2000 rpm in increments of 400 rpm were obtained.

Figures and Tables

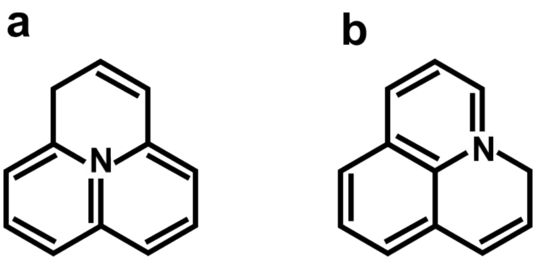

Fig. S1 Models of nitrogen positions in the structure; (a) center-N and (b) valley-N.

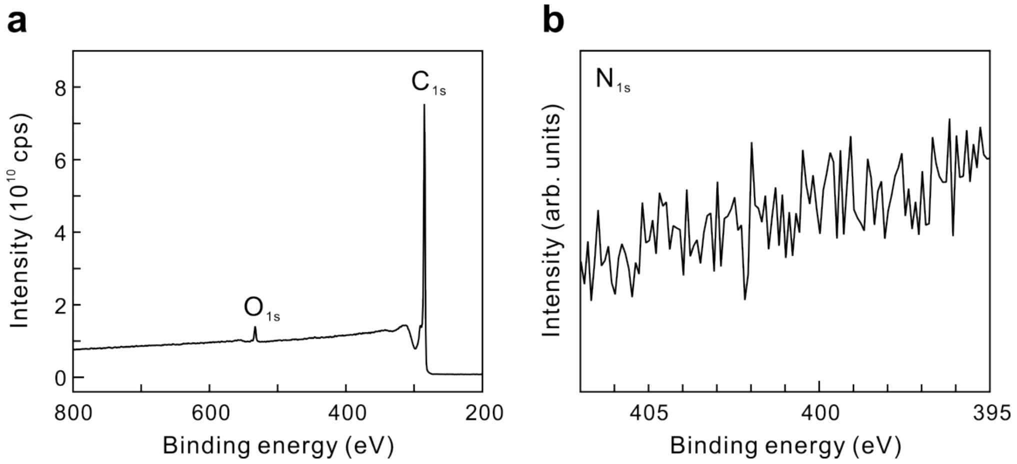

Fig. S2 (a) Wide-range and (b) narrow N_{1s} XPS spectra of the hc-SWCNTs reacted with NH_3 gas at 500 °C.

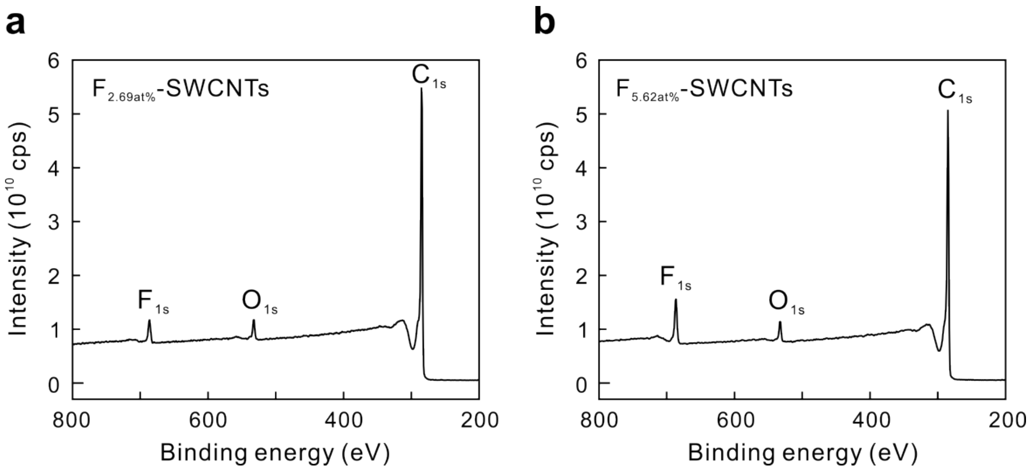

Fig. S3 Wide-range XPS spectrum of the (a) F$_{2.69at\%}$- and (b) F$_{5.62at\%}$-SWCNTs.

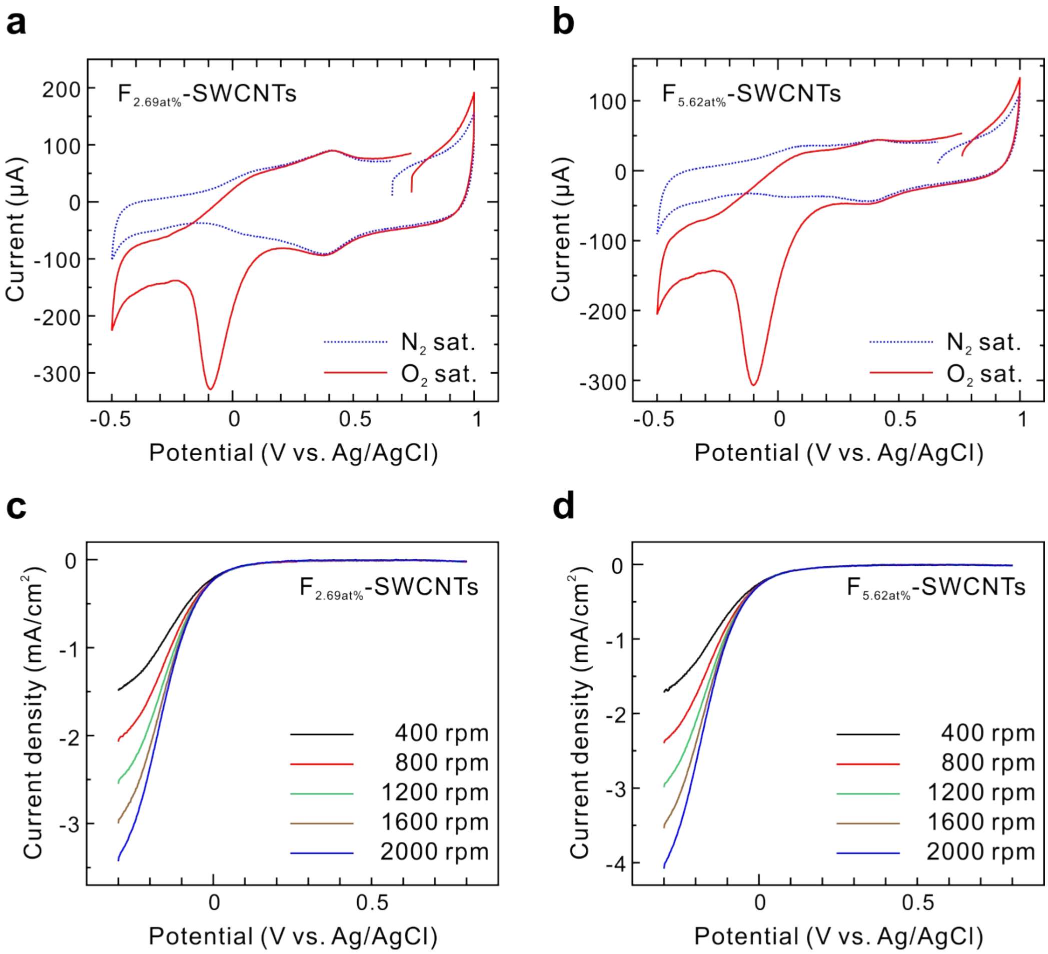

Fig. S4 CV curves of the (a) F$_{2.69at\%}$- and (b) F$_{5.62at\%}$-SWCNTs/GC electrodes in N$_2$-saturated and O$_2$-saturated 0.5 M H$_2$SO$_4$ electrolyte (scan rate: 10 mV s^{-1}). RDE curves for oxygen reduction with (c) F$_{2.69at\%}$- and (d) F$_{5.62at\%}$-SWCNTs on GC electrodes in O$_2$-saturated 0.5 M H$_2$SO$_4$ electrolyte (scan rate: 10 mV s^{-1}, rotation rate: 400–2000 rpm in increments of 400 rpm).

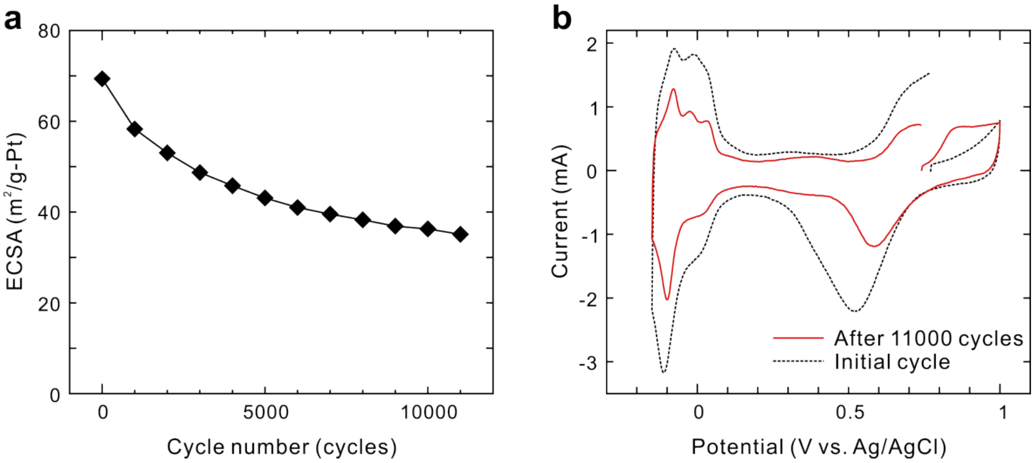

Fig. S5 (a) ECSA of the Pt-C catalyst versus cycle number. (b) Cyclic voltammograms of Pt-C catalytic electrode in N_2-saturated 0.5 M H_2SO_4 electrolyte before (black) and after (red) the durability test (scan rate: 10 mV s^{-1}).

Table S1. Chemical composition of the hc-SWCNTs reacted with NH_3 gas at 500 °C.

Samples	Chemical composition (at%)			
	C	O	N	F
hc-SWCNTs reacted with NH_3 at 500 °C	97.96	2.04	0.00	0.00

Table S2. Chemical composition of the $F_{2.69at\%}$- and $F_{5.62at\%}$-SWCNTs.

Samples	Chemical composition (at%)			
	C	O	N	F
$F_{2.69at\%}$-SWCNTs	94.45	2.86	0.00	2.69
$F_{5.62at\%}$-SWCNTs	91.14	3.24	0.00	5.62

Table S3. E_{peak}, j_{peak}, E_{onset}, $j@E_{1/2}$, and n values involved in ORR for the $F_{2.69at\%}$- and $F_{5.62at\%}$-SWCNTs catalysts.

Materials	CV		RDE			
	E_{peak} (V)	j_{peak} (mA cm^{-2})	E_{onset} (V)	j @$E_{1/2}$ (mA cm^{-2})	n	
$F_{2.69at\%}$-SWCNTs	-0.09	-0.94	+0.23	ND[a]	ND[b]	2.46[c]
$F_{5.62at\%}$-SWCNTs	-0.10	-0.89	+0.27	ND[a]	ND[b]	2.50[c]

The superscript "a" indicates "no estimation" because the limit diffusion current density cannot be observed.

The superscript "b" indicates "no estimation" because the linear correlation of the Koutecky-Levich plot at a potential of -0.1 V cannot be provided.

The superscript "c" indicates values taken at a potential of -0.3 V.

References

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