Electronic Supplementary Information for

Selective Electrocatalysis of Nitrous Oxide Reduction Reaction to Nitrogen at Carbon-Supported Pt–Pd–Sn Nanoparticles

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EXPERIMENTAL SECTION

Materials

Ethanol, hexane, 2-propanol, perchloric acid, oleylamine, butylamine, [Pt(acac)$_2$] (acac = acetylacetonato), and 5% Nafion DE520 were purchased from Wako Pure Chemical Industries, Ltd. Borane-morpholine complex, tin(II) chloride dihydrate (SnCl$_2$·2H$_2$O), and [Pd(acac)$_2$] were commercially available from TCI, Kanto Chemical Co., Inc., and Sigma-Aldrich, respectively. Vulcan XC-72R carbon black was bought from Cabot Corporation. Pure argon gas (99.9995%, Hokkaido Air Water), nitrous oxide gas (99.99%, Hokkaido Air Water), and pure oxygen gas (99.995%, Air Liquide Japan) were used for electrochemical measurements.

Synthesis of Pt–Sn and Pt–Pd–Sn nanoparticles

Pt–Sn and Pt–Pd–Sn nanoparticles (NPs) were synthesized in a modified method based on a reported synthetic procedure.[1] Pt–Pd–Sn NPs with Pt:Pd:Sn = 45:30:25 (precursor-based atomic%) were synthesized as the optimized Pt:Pd = 3:2 = 45:30 atomic ratio was obtained from our previous study.[2] In this case, [Pt(acac)$_2$] (28.3 mg, 0.072 mmol), [Pd(acac)$_2$] (14.6 mg, 0.048 mmol), and OAm (15 mL) were mixed under ultrasonication for 10 min in a three-necked round bottom flask (100 mL), yielding a suspension. The suspension was purged with Ar and then stirred in an oil bath at 333 K under Ar to get a transparent solution with a pale yellow color. In a glass vial, 100 mg of borane-morpholine complex (BM) (0.99 mmol) was dissolved in 3 mL of OAm under ultrasonication, and the solution was quickly injected into the pre-heated precursor solution at 333 K to initiate the nucleation of Pt–Pd NPs. Then, the temperature was raised to 363 K, and the color of the mixture changed completely to black. The mixture was kept at 363 K for 30 min for the formation of Pt–Pd seed NPs. After that, the temperature of the mixture was raised to 453 K for the growth of the NPs. In a glass vial, 9 mg of SnCl$_2$·2H$_2$O (0.04 mmol) was dissolved in 3 mL of OAm under ultrasonication, and the solution was quickly injected into the reaction mixture at 453 K. The mixture was kept at 453 K for 30 min for the formation of Pt–Pd–Sn NPs. After the mixture was cooled naturally to room temperature, Pt–Pd–Sn NPs were separated by adding ca. 160 mL of ethanol and centrifugation at 12,000 rpm at 298 K for 10 min using a Micro Refrigerated

Centrifuge 3700 equipped with an angle rotor AF-5004CA (Kubota Co.). The Pt–Pd–Sn NPs were further washed with ca. 30 mL of ethanol–hexane solvent mixture (8:2, *v/v*) eight times under centrifugation at 10,000 rpm at 298 K for 5 min each and finally stored in ethanol at room temperature until use. Similarly, the Pt–Pd NPs were synthesized without the addition of $SnCl_2·2H_2O$.

Pt–Sn NPs with Pt:Sn = 75:25 (precursor-based atomic%) were synthesized in a similar synthetic procedure of Pt–Pd–Sn NPs by replacing atomic% of Pd by Pt. [Pt(acac)$_2$] (47.2 mg, 0.12 mmol) and OAm (15 mL) were mixed under ultrasonication in a three-necked round bottom flask (100 mL) to get a suspension. Next, the steps are as same as the steps of the synthesis of Pt–Pd–Sn NPs. Pt NPs were synthesized in a similar synthetic procedure of Pt–Sn NPs without using $SnCl_2·2H_2O$.

Preparation of carbon-supported Pt–Sn and Pt–Pd–Sn NPs

To prepare carbon-supported catalysts with a 20:80 metal-to-carbon ratio, Vulcan XC-72R carbon black (ca. 1.2 mg) and Pt–Sn or Pt–Pd–Sn NPs (ca. 0.3 mg) were dispersed in 10 mL of butyleamine (BAm) in order to remove OAm and immobilize NPs on the carbon support. The mixture was ultrasonicated for one hour and then stirred at 200 rpm for three days. After that, the mixture was collected by centrifugation at 12,000 rpm for 10 min. The precipitate was washed with ethanol (ca. 10 mL) two times at 10,000 rpm for 7 min and then re-dispersed in the mixture of 900 µL of 2-propanol and 1600 µL of Milli-Q water. The dispersion was transferred into a 5 mL glass vial, and 10 µL of 5% Nafion DE520 was added. Then, the dispersion was ultrasonicated in a water bath at 298 K for three hours to obtain catalyst ink of carbon-supported Pt–Sn or Pt–Pd–Sn NPs (Pt–Sn/C or Pt–Pd–Sn/C). The prepared ink was used in one day for the preparation of working electrodes.

Catalyst characterizations

Transmission electron microscopy (TEM) images were taken by a JEM-2000FX (JEOL) at an acceleration voltage of 200 kV. High-angle annular dark field-scanning transmission electron microscopy (HAADF-STEM) and energy dispersive spectroscopy

(EDS) elemental mapping images were taken by a JEM-ARM200F (JEOL) at an acceleration voltage of 200 kV.

X-ray powder diffraction (XRD) was performed on a BRUKER D2 PHAGER 2nd Gen diffractometer with Cu Kα radiation (λ = 0.154 nm).

Inductively coupled plasma mass spectrometry (ICP-MS) measurements were performed using an ICP-MS spectrometer 8800 ICP-QQQ (Agilent Technologies). For sample preparation of ICP-MS, a catalyst ink (30 µL) was dispersed in 3 mL of aqua regia solution, and then the dispersion was stirred at 308 K for at least 24 h. The dispersion was filtered through a membrane filter (13HP045AN, ADVANTEC), and then the filtrate was diluted with aqua regia up to the mark of a 10 mL volumetric flask.

X-ray photoelectron spectroscopy (XPS) data were collected at the pass energy of 10 eV using an Al Kα X-ray source by a photoelectron spectrometer JPS-9200 (JEOL). The binding energy was calibrated using C 1s peak at 284.7 eV. To prepare the sample for XPS, catalyst ink of carbon (ca. 1.2 mg)-supported NPs (ca. 0.6 mg) in 2-propanol without Nafion was dropcasted on a carbon tape (ca. 1 cm in length), and the solvent was evaporated at 373 K.

Sn K-edge X-ray absorption spectroscopy (XAS) was performed at the beamline BL14B2 in SPring-8. XAS data of a Sn foil, a pellet of SnO diluted in boron nitride (BN) and a pellet of SnO_2 diluted in BN as reference samples were collected in a transmission method. XAS data of catalysts were collected in a fluorescent method using a 19 Ge-element solid state detector (SSD). For sample preparation, a catalyst ink (235 µL) was dropcasted onto a carbon sheet of PERMA-FOIL (PF-20UHP; 0.2 mm in thickness; TOYO TANSO) at 323 K with a geometrical area of 0.50 cm^2 (a circle with a diameter of 8 mm) using a tape (N-380, Nitto Denko) with a hole with the same area. After the removal of the tape, the catalyst on the carbon sheet was heated at 418 K for 5 min. For XAS measurements in the fluorescent method, the sheet with the catalyst was held using a spectroelectrochemical flow cell.[3,4] The sample was placed at 45º to the X-ray stream and the SSD. Extended X-ray absorption fine structure oscillation values, $\chi(k)$, in the k range from 3 to 12 Å^{-1} were extracted from XAS data. The $k^3\chi(k)$ values were Fourier-transformed into R-space, followed by the inverse Fourier transform into k-space using the software package REX2000 (Rigaku).[5–7]

Electrochemical measurements

Electrochemical measurements were performed using a conventional three-electrode, one-compartment electrochemical cell by a potentiostat HZ-7000 (Hokuto Denko Corp.). A platinized Pt foil and an Ag|AgCl (sat. KCl) were used as the counter and the reference electrodes, respectively. A glassy carbon (GC) plate ($25 \times 25 \times 2$ mm^3, ALS Co., Ltd.), on which the catalyst was dropcasted, was used as the working electrode.

The GC plate was polished with alumina slurry (0.3 μm, Baikalox), followed by alumina slurry (0.05 μm, Baikalox), and then sonicated in water, ethanol, and Milli-Q water for 5 min each. A tape (N-380, Nitto Denko) with a prepared hole of 8 mm in diameter was placed on the GC plate to control the surface area of the working electrode. Thus, the geometrical surface area of the working electrode was controlled to be 0.50 cm^2. For all catalysts, the ink (43~50 μL) was dropcasted on the hole so that the metal loading was 11.2 μg cm^{-2}, and then dried at 313 K for 20 min.

Cyclic voltammograms (CVs) were recorded in an aqueous solution of 0.1 M HClO$_4$. Before measurements of CVs, the electrolyte solution was purged with Ar for at least 30 min. For electrochemical cleaning, three potential cycles at 200 mV s^{-1} were performed in the potential range between –0.2 and +1.1 V vs. Ag|AgCl (sat. KCl) (ca. +0.05 and +1.4 V vs. reversible hydrogen electrode (RHE)) in a 0.1 M HClO$_4$ aqueous solution under Ar before recording CVs at 50 mV s^{-1}. For the electrochemical N$_2$O reduction, a 0.1 M HClO$_4$ aqueous solution in an electrochemical cell (VM3A, EC Frontier Co., Ltd.) was saturated with bubbling of N$_2$O gas at 10 mL min^{-1} for 30 min, and then the CVs were recorded under N$_2$O at a sweep rate of 10 mV s^{-1}. The first cycle of the CVs is always shown in this work. All potentials vs. Ag|AgCl (sat. KCl) were converted to those against the RHE by using the following equation: E (vs. RHE) = E (vs. Ag|AgCl (sat. KCl)) + 0.199 + 0.059 × pH.

Electrolysis experiments in acidic media under N$_2$O in the absence or presence of O$_2$ were conducted with an H-type electrolytic cell (VB12A, EC Frontier Co., Ltd.) separated by a Nafion NRE-211 (DuPoint) membrane. The Nafion membrane was boiled in 3% H$_2$O$_2$ at 353 K for 1 h, in Milli-Q water at 373 K for 1 h, in 1 M H$_2$SO$_4$ at 353 K for 1 h, and then in Milli-Q water at 373 K for 1 h, sequentially. A working electrode with Pt–Sn/C or Pt–Pd–Sn/C ink was prepared on both sides of a GC substrate of 5.38 cm^2

geometrical area by dropcasting the ink with metal loading 11.2 µg cm^{-2}. The working electrode and the Ag|AgCl (sat. KCl) reference electrode were placed in the cathodic chamber, and a platinized Pt foil as the counter electrode was placed in the anodic chamber. 25 mL of a 0.1 M HClO$_4$ aqueous solution was added in each chamber, and only the solution in the cathodic chamber was saturated with bubbling of N$_2$O or N$_2$O–O$_2$ mixtures of 1:0.2, 1:0.4, 1:1, and 1:10 N$_2$O to O$_2$ molar ratios for 30 min at 10 mL min^{-1} after pursing the solution with Ar for 30 min. Chronoamperometry (CA) was performed at 0 V, +0.06 V, and +0.12 V vs. RHE for 1 h for the detection of gaseous products of N$_2$ and/or H$_2$.

Gaseous product detection and quantification

The gaseous products were analyzed by gas chromatography (GC-8A, SHIMADZU) equipped with a thermal conductivity detector (TCD) at a constant column temperature of 323 K and a detector temperature of 423 K. The chromatographic column was a Shincarbon-ST 50/80 and an Ar stream was the carrier gas flowing at a constant pressure of 0.5 MPa. Headspace gas of 100 µL was collected by a gas-tight syringe from the headspace of the cathodic chamber after 1 h of electrolysis and introduced into the GC–TCD for the detection of N$_2$ and/or H$_2$. The retention times of H$_2$ and N$_2$ were ca. 3.4 and 9.3 min, respectively. The air-tightness of the electrochemical cell was confirmed by GC–TCD after conducting a blank experiment under Ar. For the quantification of N$_2$, an external calibration was carried out using pure N$_2$ gas with 3 to 50 µL. For the calibration curve of H$_2$, 10 ~ 90 µL of a mixture of H$_2$ and Ar with a 1:9 (v/v) ratio was injected into the GC–TCD. The number of moles (n) of N$_2$ or H$_2$ was calculated using the following Eq. (1):

$$n = \frac{pV_i}{RT} \qquad (1)$$

where p is the pressure of the gas (p = 101325 Pa), R is the gas constant (R = 8.314 J mol^{-1} K^{-1}) and T is the absolute temperature of the gas (298.15 K), and V_i is the injected volume (L) of N$_2$ or H$_2$ into the GC–TCD. Plots of peak areas against the number of moles of N$_2$ or H$_2$ in the H$_2$–Ar mixture showed a linear relationship with R^2 = 0.9999 (**Fig. S1**). Using the calibration curves, the number of moles of N$_2$ and H$_2$ each present in

100 µL of headspace was calculated, and then the total number of moles of N_2 or H_2 present in the headspace after the electrolysis was determined.

The number of moles of N_2 and/or H_2 present in the solution was calculated based on Henry's law in Eq. (2):[8]

$$c = H^{cp} \times p$$

$$\text{Or } n = H^{cp} \times p \times V_s \qquad (2)$$

where c is the solubility (mol L^{-1}) of a gas in the solution, p is the partial pressure (Pa) of the gas in the headspace under equilibrium conditions, H^{cp} is Henry's law solubility constant ($H^{cp} = 6.4 \times 10^{-9}$ mol L^{-1} Pa^{-1} for N_2 and 7.7×10^{-9} mol L^{-1} Pa^{-1} for H_2), n is the number of moles of the gas in the solution, and V_s is the volume (L) of the solution in the cathodic chamber. The p of the gas was calculated using Eq. (1) when V_i is assigned as the volume of the headspace.

The total number of moles of produced N_2 or H_2 (n_N_2 [mol] or n_H_2 [mol]) in the cathodic chamber allowed us to calculate Faradaic efficiency (FE) for each of them using Eq. (3):

$$\text{FE} = \frac{n\_N_2 \text{ [mol] or } n\_H_2 \text{ [mol]} \times F \times 2}{Q} \times 100 \qquad (3)$$

where F is the Faradaic constant ($F = 96485$ C mol^{-1}), Q is the total charges (C) obtained from 1 h of electrolysis, and 2 is the number of electrons required for the N_2O reduction to N_2 or the proton reduction to H_2 (the hydrogen evolution reaction).

The turnover frequency (TOF) of produced N_2 or H_2 in the cathodic chamber after 1 h of electrolysis was calculated using Eq. (4):[9,10]

$$\text{TOF} = \frac{n\_N_2 \text{ [mol] or } n\_H_2 \text{ [mol]}/t \text{ [min]}}{n\_\text{noble metals [mol]}} \qquad (4)$$

where n_N_2 [mol] and n_H_2 [mol] are the number of moles of the N_2 and H_2, respectively, generated after $t = 60$ min electrolysis, $n\_$noble metals is the number of moles of noble metals involved in the production of n_N_2 [mol] and/or n_H_2 [mol].
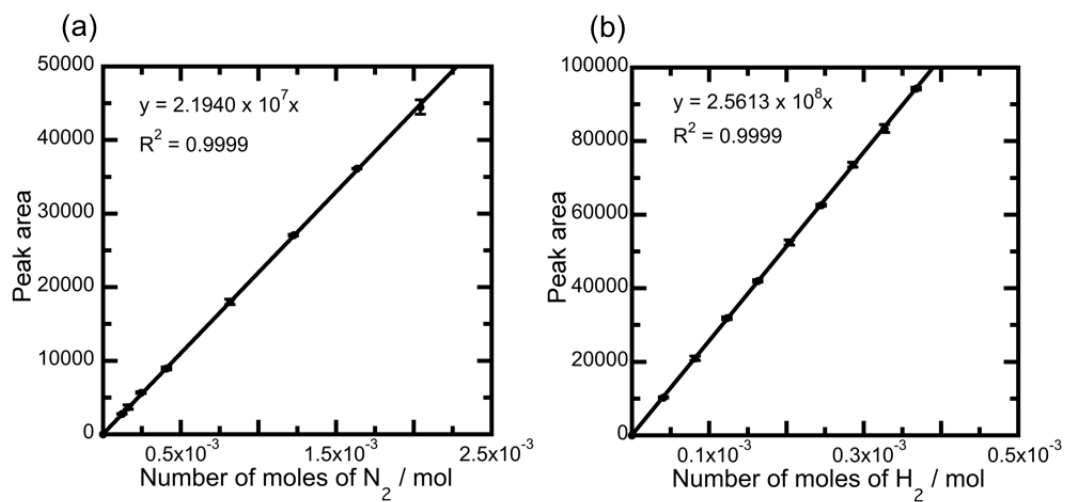
Fig. S1 The peak area-mole calibration curves of (a) N_2 and (b) H_2 obtained from gas chromatography.
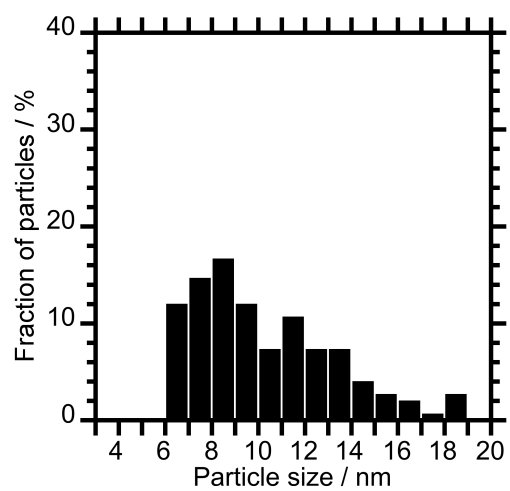
Fig. S2 Size distribution of Pt–Pd–Sn NPs in Pt–Pd–Sn/C obtained from the TEM image in **Fig. 2(a)**.
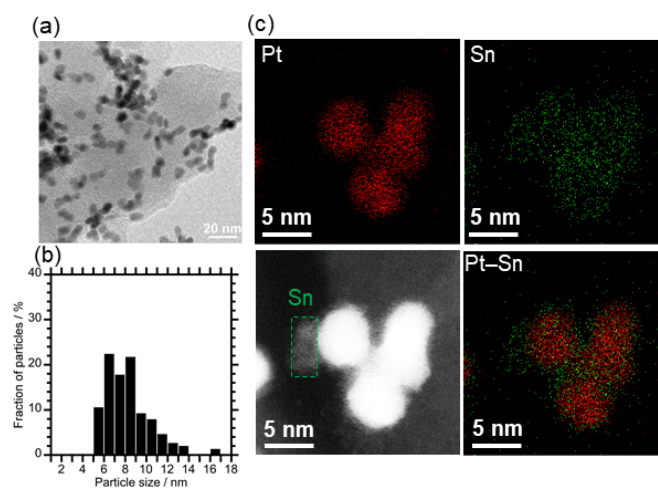
Fig. S3 (a) TEM image, (b) size distribution, and (c) HAADF-STEM and EDS elemental mapping images of Pt–Sn/C. The red and green dots indicate the Pt and Sn elements, respectively.
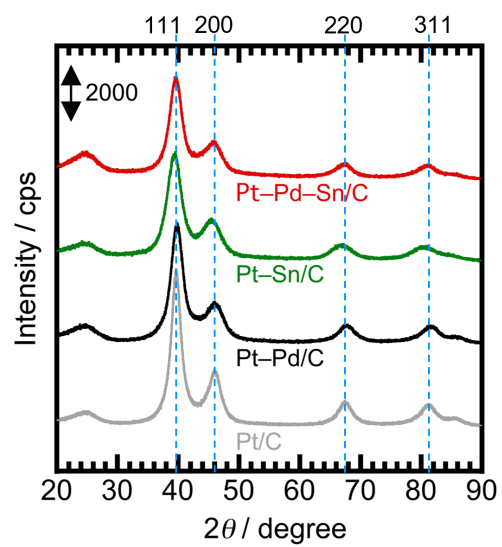
Fig. S4 XRD patterns of Pt–Pd–Sn/C (in red), Pt–Sn/C (in green), Pt–Pd/C (in black), and Pt/C (in gray).
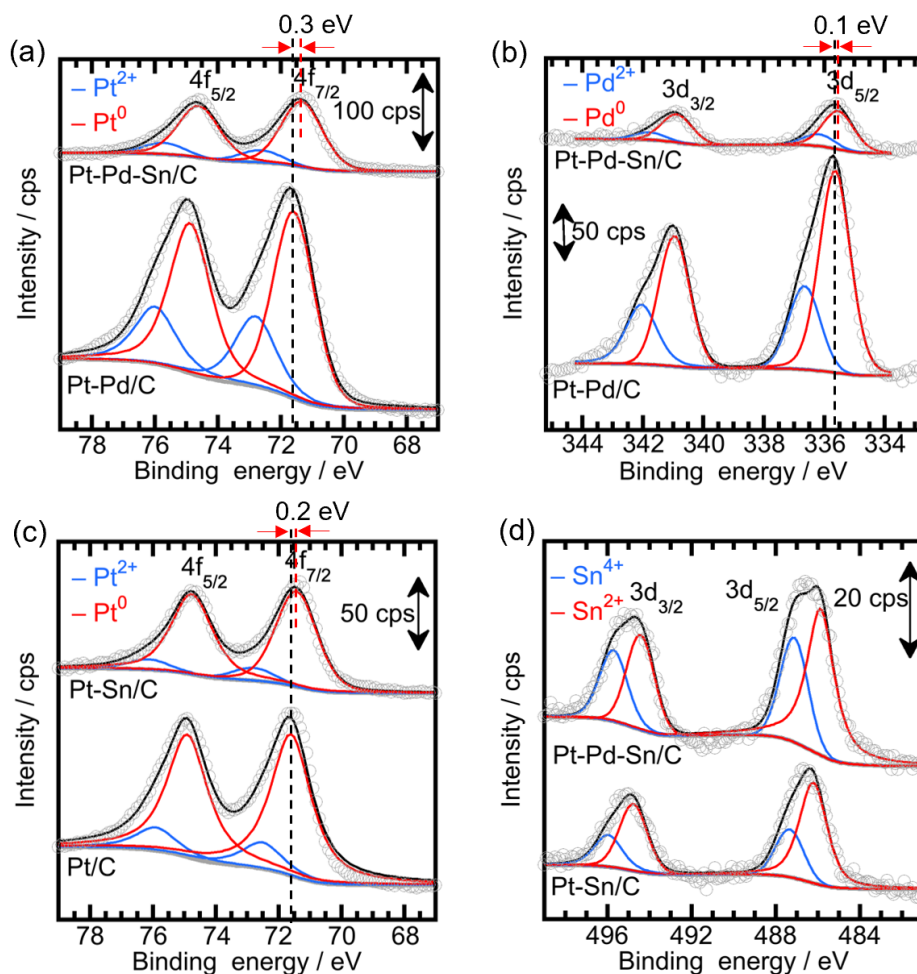
Fig. S5 XPS data of Pt–Pd–Sn/C and Pt–Pd/C in the (a) Pt 4f, (b) Pd 3d, and (d) Sn 3d regions, and Pt–Sn/C and Pt/C in the (c) Pt 4f and (d) Sn 3d regions. Experimental data (open circles), the sum of the deconvoluted data (the solid lines in black), and baselines (in gray); Pt^0 species (the solid lines in red) and Pt^{2+} species (the solid lines in blue) in (a) and (c), Pd^0 species (the solid lines in red) and Pd^{2+} species (the solid lines in blue) in (b), and Sn^{2+} species (the solid lines in red) and Sn^{4+} species (the solid lines in blue) in (d).
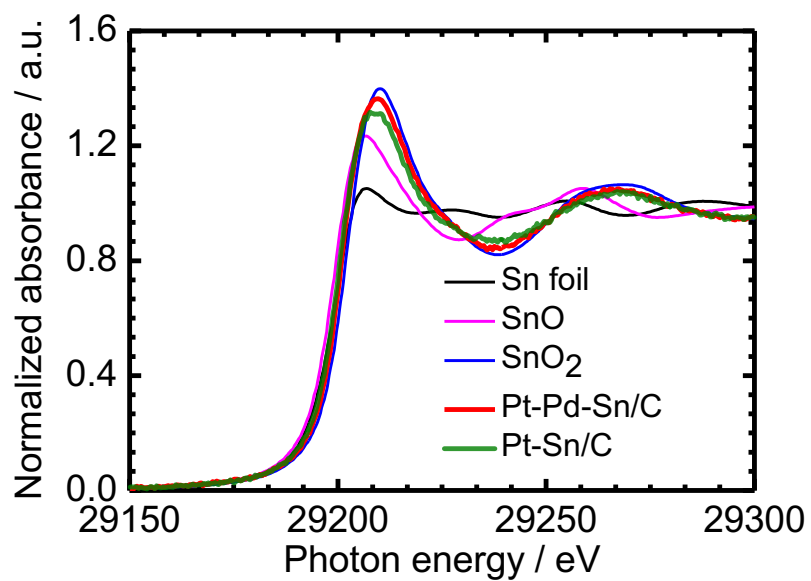
Fig. S6 Sn *K*-edge XAS data of catalysts of Pt–Pd–Sn/C (in red) and Pt–Sn/C (in green) and reference samples of SnO_2 (in blue), SnO (in pink), and Sn-foil (in black). The data of the catalysts were recorded in the fluorescent method and the data of the reference samples were collected in the transmission method. The data were collected at the beamline BL14B2 in SPring-8.
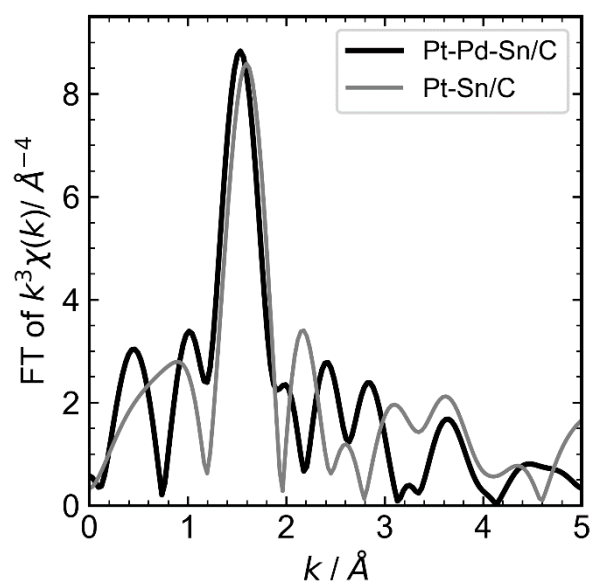
Fig. S7 Fourier transforms of extended X-ray absorption fine structure oscillations of Pt–Pd–Sn/C (black) and Pt–Sn/C (gray) in the Sn K-edge region.
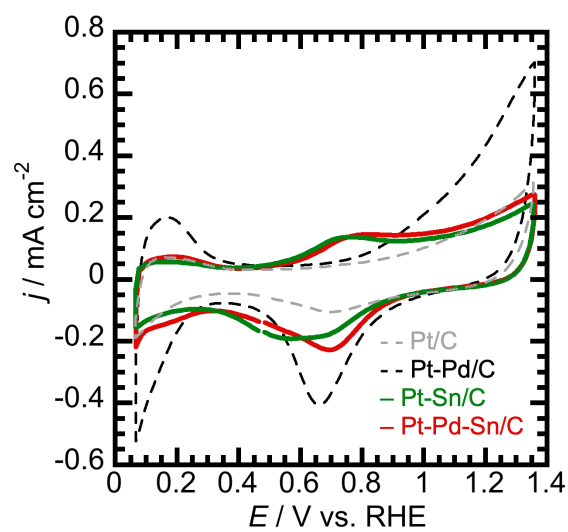
Fig. S8 CVs of Pt–Pd–Sn/C (red solid line), Pt–Sn/C (green solid line), Pt–Pd/C (black broken line), and Pt/C (grey broken line) in a 0.1 M HClO$_4$ aqueous solution at a sweep rate of 50 mV s^{-1} under Ar.
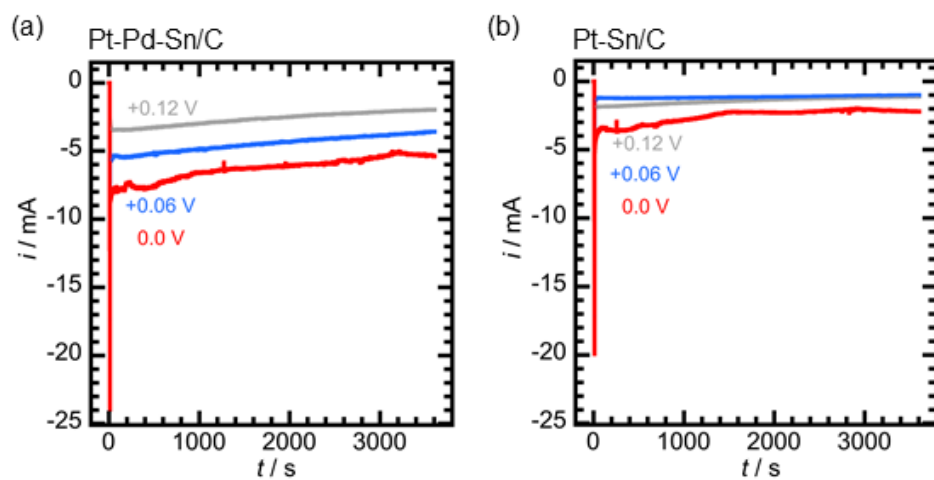
Fig. S9 Chronoamperometry of (a) Pt–Pd–Sn/C and (b) Pt–Sn/C in a 0.1 M $HClO_4$ aqueous solution under N_2O in the absence of O_2 for 1 h at 0, +0.06, and +0.12 V vs. RHE at room temperature and atmospheric pressure.
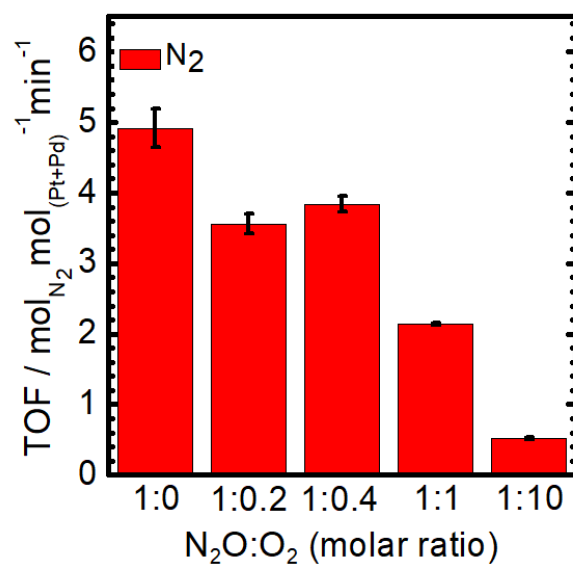
Fig. S10 TOFs of N_2 obtained from N_2ORR in a 0.1 M $HClO_4$ aqueous solution under different molar ratios of the N_2O–O_2 mixture at Pt–Pd–Sn/C at +0.06 vs. RHE at room temperature and atmospheric pressure.

Table S1 Diffraction angles of the Pt–Pd–Sn/C, Pt–Sn/C, Pt–Pd/C, and Pt/C in **Fig. S4**. The Cu *K*α radiation (*λ* = 0.154 nm) was used for all measurements.

Catalysts	2θ / degree			
	111	200	220	311
Pt–Pd–Sn/C	39.6	45.8	67.4	81.3
Pt–Sn/C	39.5	45.4	67.3	80.9
Pt–Pd/C	39.8	46.0	67.5	81.6
Pt/C	39.6	46.0	67.4	81.3

Table S2 Summary of curve fit parameters of Sn *K*-edge FT-EXAFS oscillations of Pt–Pd–Sn/C and Pt–Sn/C for Sn-O bonds. C.N. and D. W. factors indicate coordination number and Debyle Waller factors, respectively.

Catalysts	C.N. (Sn-O)	Bond distance /Å	D.W. factor/ Å	*R*-factor / %
Pt–Pd–Sn/C	6.0±0.9	2.03±0.01	0.09±0.02	2.7
Pt–Sn/C	4.7±0.7	2.06±0.01	0.06±0.02	2.3

Table S3 FEs of N_2 and H_2 obtained from N_2ORR at Pt–Pd–Sn/C and Pt–Sn/C after 1 h electrolysis at 0, +0.06, and +0.12 V vs. RHE under N_2O in the absence of O_2 at room temperature and atmospheric pressure.

Catalysts	FE / %			
	0 V vs. RHE		+0.06 V vs. RHE	+0.12 V vs. RHE
	H_2	N_2	N_2	N_2
Pt–Pd–Sn/C	11±7	75±6	90±2	91±1
Pt–Sn/C	30±15	64±18	94±1	96±2

Table S4 TOFs of N_2 and H_2 obtained from N_2ORR at Pt–Pd–Sn/C and Pt–Sn/C after 1 h electrolysis at 0, +0.06, and +0.12 V vs. RHE under N_2O in the absence of O_2 at room temperature and atmospheric pressure.

Catalysts	TOF / $mol_{N_2 or H_2} mol_{(Pt+Pd)}^{-1} min^{-1}$			
	0 V vs. RHE		+0.06 V vs. RHE	+0.12 V vs. RHE
	H_2	N_2	N_2	N_2
Pt–Pd–Sn/C	0.81±0.50	5.85±0.74	4.92±0.27	2.85±0.04
Pt–Sn/C	0.91±0.69	1.72±0.08	1.30±0.21	1.83±0.04

Table S5 FEs and TOFs of N_2 obtained from N_2ORR at Pt–Pd–Sn/C after 1 h of electrolysis at +0.06 vs. RHE under different O_2 content in the N_2O–O_2 mixture at room temperature and atmospheric pressure.

$N_2O:O_2$ (molar ratio)	FE / %	TOF / $mol_{N_2} mol_{(Pt+Pd)}^{-1} min^{-1}$
1:0	90±2	4.92±0.27
1:0.2	86±3	3.56±0.14
1:0.4	79±2	3.84±0.11
1:1	71±1	2.14±0.02
1:10	44±1	0.52±0.02

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