

## Supporting information

### Continuous syntheses of carbon-supported Pd and Pd@Pt core–shell nanoparticles using flow-type single-mode microwave reactor

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## Experimental

### Chemicals

For use in this study, Na<sub>2</sub>[PdCl<sub>4</sub>] (98%) and Vulcan XC-72 were purchased respectively from Aldrich Chemical Co. Inc. and Cabot Corp. Also, H<sub>2</sub>[PtCl<sub>6</sub>]·6H<sub>2</sub>O (98.5%), NaOH (97%), NaBr (99%), ethylene glycol (EG), Nafion<sup>®</sup> (DE520 CS, 5%), and HClO<sub>4</sub> (60%) were purchased from Fujifilm Wako Pure Chemical Corp.

### Microwave reactor system

The MW reactor is composed mainly of a variable-frequency MW generator (2.3–2.7 GHz, 100 W) using a solid-state device and a cylindrical TM<sub>010</sub> single-mode cavity.<sup>26, 30</sup> A PTFE tube with 1 mm inner diameter was placed on the cylinder center axis where the electric field was concentrated. The reaction solution was passed internally. The PTFE tube surface temperature was measured using a radiation thermometer and was taken as the reaction solution temperature. To change the optimum MW frequency based on the temperature change of the solution, the MW frequency and

applied power were controlled using a feedback module incorporating a microcomputer. We designate this microwave heating apparatus as a frequency-synchronized microwave reactor (*Symwave reactor*).

### ***Flow synthesis of carbon-supported Pd and Pd@Pt core–shell nanoparticles***

A schematic view of the process for the continuous synthesis of carbon-supported Pd and Pd@Pt core–shell nanoparticles is presented in Fig. 1. We attempted to conduct a series of reactions coherently in a flow reaction system, i.e., MW-assisted flow reaction for the synthesis of carbon supported core Pd nanoparticles, followed by deposition of Pt shell. Typically, a mixture containing of  $\text{Na}_2[\text{PdCl}_4]$  (1–4 mM) in EG, carbon support (Vulcan XC72, 0.1 wt%) and an aqueous NaOH solution (5 M) were prepared. This mixture was introduced continuously into the PTFE tube reactor placed in the center of MW cavity. EG works as the reaction solvent as well as the reducing agent that converts Pd(II) into Pd(0) nanoparticles. The MW heating temperature was set at 100 °C with the flow rate of 80 ml h<sup>-1</sup>, which corresponds to residence time of 4 s. The carbon-supported Pd nanoparticles were transferred directly to the Pt shell formation process without particle isolation. The dispersed solution was introduced into T-type mixer and was mixed with a EG solution of  $\text{H}_2[\text{PtCl}_6] \cdot 6\text{H}_2\text{O}$  (10 mM). The molar ratio of Pd : Pt was fixed to 1 : 1. Subsequently, aqueous NaOH solution was mixed at the second T-mixer. Then the reaction mixture was taken out of the mixer and let to stand at room temperature (1–72 h) for Pt shell growth.

### ***Flow synthesis of carbon-supported Pd nanoparticles by adding NaBr***

A mixture containing  $\text{Na}_2[\text{PdCl}_4]$  (5 mM) in EG, carbon support (Vulcan XC72, 0.1 wt%), and aqueous NaBr solution (5 M) were prepared. This mixture was introduced continuously into the PTFE tube reactor placed in the center of MW cavity. The MW heating temperature was set at 100 °C with the flow rate of 80 ml h<sup>-1</sup>, which corresponds to residence time of 4 s.

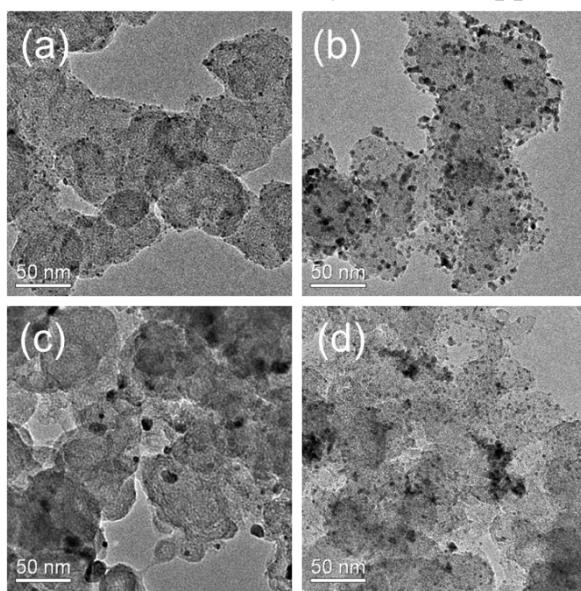
### ***Analysis of Pd and Pd@Pt core–shell nanoparticles***

The nanoparticle sizes were determined using transmission electron microscopic (TEM, Tecnai G2; FEI Co.) images. TEM samples were prepared by dropping nanoparticle dispersions onto a carbon film supported

by the Cu grid. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and energy dispersive X-ray spectrometry (EDS) analysis of Pd@Pt core–shell nanoparticles were applied (JEM-ARM200F; JEOL Ltd.). The Pd and Pt concentrations were measured using an ICP-optical emission spectrophotometer (ICP-OES, SPS3100; SII).

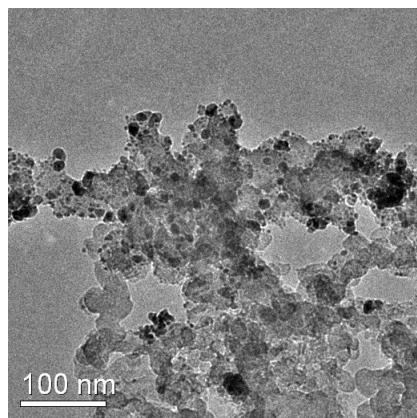
### ***Electrochemical characterization***

The obtained catalyst was purified repeatedly by centrifugation to remove EG and other materials and thereby to obtain a catalyst ink having 0.0125 wt% carbon concentration and 0.0125 wt% Nafion concentration. As the catalyst ink solvent, a mixed solvent of water and isopropanol (weight ratio 3:1) was used. After we applied 20  $\mu$ L of this catalyst ink to a 5-mm-diameter ground glassy carbon rotating electrode, we used it for electrochemical measurements. As the electrolyte, we used 0.1 M  $\text{HClO}_4$ . A reversible hydrogen electrode was used as the reference electrode. The catalyst surface was cleaned by potential scanning at 0.05–1.2 V in an electrolytic cell in which oxygen was blown off by bubbling nitrogen. The electrochemically active surface area was measured from the adsorption/desorption peak shape. Subsequently, oxygen was dissolved until saturated in the electrolytic solution by bubbling. Convective voltammetry was performed by rotating the electrode at 1600 rpm. The oxygen reduction activity was measured. The scanning speed was 20 mV  $\text{s}^{-1}$  from the low potential side to the high potential side. The oxygen reduction current value at 0.9 V was recorded. The oxygen reduction activity of the catalyst was calculated from the Koutechy–Levich formula. The electrolyte temperature at the time of activity measurement was 25 °C. Oxygen reduction activity was calculated in the form of oxygen reduction current per unit of Pt weight. In the potential cycle in the durability test, a square wave of 0.6 V for 3 s and 1.0 V for 3 s was taken as one cycle. Potential of 5000 cycles was applied at 25 °C. The surface area and the activity were measured in the described above manner before and after the potential cycle.

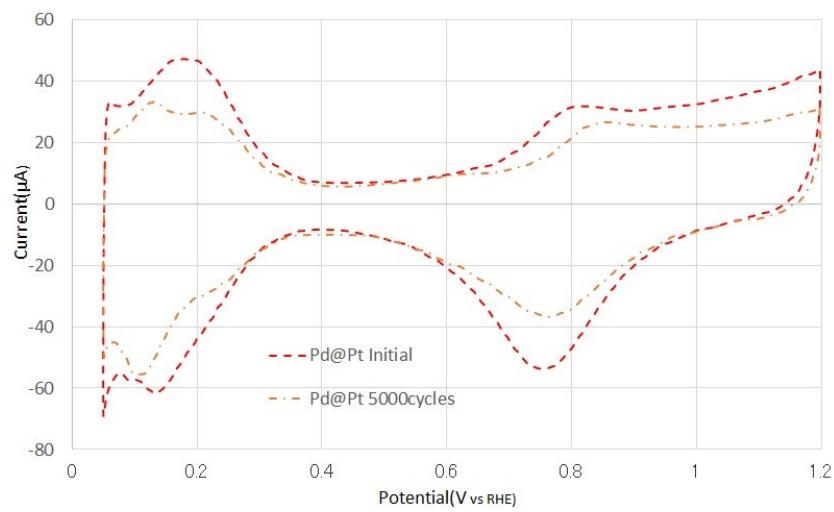
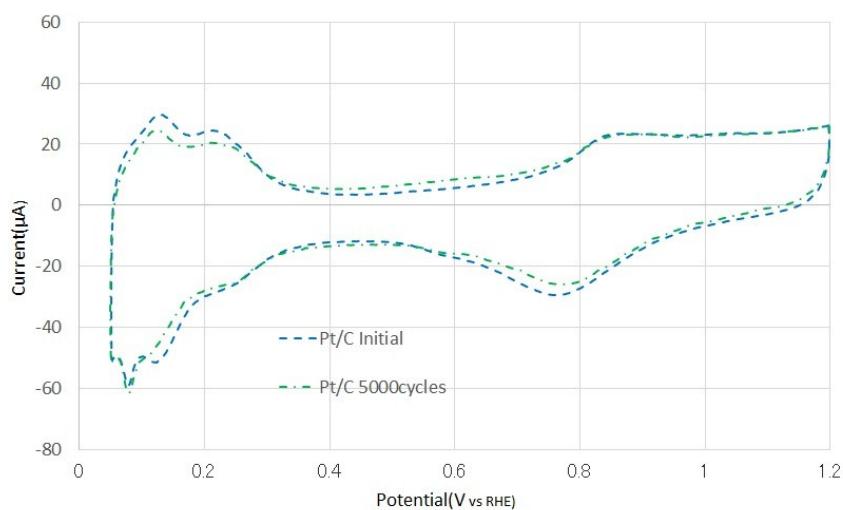
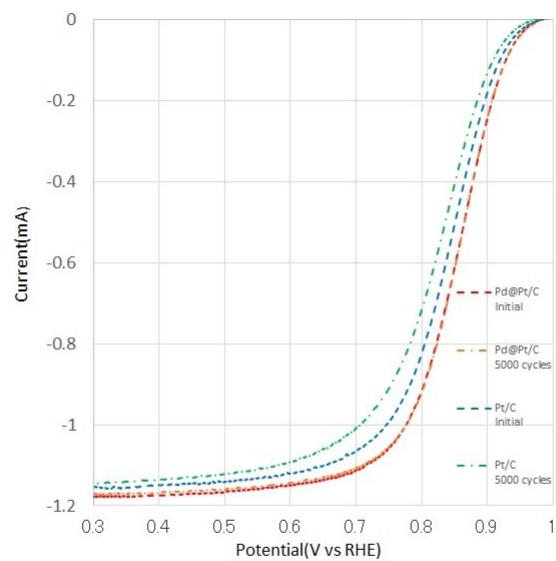


oxygen reduction measured in the described above after the potential

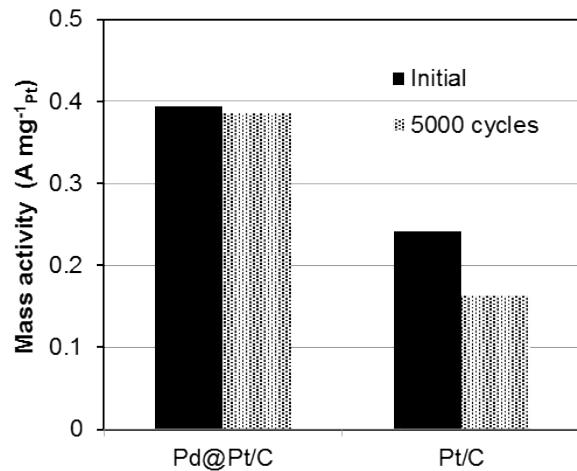
**Figure S1.** TEM images of carbon-supported Pd nanoparticles synthesized using the MW flow reactor. Concentrations of  $\text{Na}_2[\text{PdCl}_4]$  and NaOH were the following: (a) 1 mM and 10 mM, (b) 4 mM and 10 mM, (c) 2 mM and 0 mM, and (d) 2 mM and 20 mM. The respective average particle sizes were (a) 1.8 nm, (b) 4.5 nm (c) 12.3 nm, and (d) 2.6 nm.



**Figure S2.** TEM image of carbon-supported Pd nanoparticles synthesized by adding NaBr. Concentrations of  $\text{Na}_2[\text{PdCl}_4]$  and NaBr were, respectively, 5 mM and 100 mM. Although more NaBr was added than in the earlier study, cubic Pd nanoparticles were rarely confirmed.

**(a)****(b)****(c)**

(d)



**Figure S3.** Electrochemical properties of the carbon-supported Pd@Pt core–shell nanoparticles and Pt nanoparticles. For this experiment, the carbon-supported Pt nanoparticle with Pt 2 mM was prepared as a reference catalyst using a similar synthetic method. (a, b) Comparison of cyclic voltammetry curves of the catalysts in a  $\text{N}_2$ -saturated 0.1 M  $\text{HClO}_4$  solution (0.05–1.2 V, scanning rate: 50  $\text{mV s}^{-1}$ ). (c) Oxygen reduction polarization curves in an  $\text{O}_2$ -saturated 0.1 M  $\text{HClO}_4$  solution at a 20  $\text{mV s}^{-1}$  scanning rate and 1600 rpm rotation speed. (d) Comparison of Pt mass activities of carbon-supported Pd@Pt core–shell and Pt nanoparticles.