Supplementary Information

## Size-Controlled Synthesis of Mesoporous Palladium Nanoparticles as

## **Highly Active and Stable Electrocatalysts**

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## **Experimental Section**

**Chemicals:** Sodium tetrachloropalladate (Na<sub>2</sub>PdCl<sub>4</sub>), ascorbic acid, sulfuric acid, and formic acid were purchased from Nacalai. Co. Both hexadecylpyridinium chloride monohydrate (HDPC) and F127 triblock copolymers were purchased from Sigma-Aldrich. All the chemicals were used without further purification.

Synthesis of mesoporous Pd nanoparticles (MPNs): In a typical synthesis, 100 mg of hexadecylpyridinium chloride (HDPC) was dissolved in distilled water (3.0 mL). After being thoroughly dissolved, a 2 wt% F127 aqueous solution was added to the HDPC solution. After stirring for several hours to obtained homogeneous solution, 500  $\mu$ L of 40 mM sodium tetrachloropalladate (Na<sub>2</sub>PdCl<sub>4</sub>) aqueous solution, and 1000  $\mu$ L of 100 mM ascorbic acid solution were quickly added, separately. Then, the solution was further incubated in a water bath set at 40 °C for 10 hours. The resulting colloidal products were collected by centrifugation and washed several times by using ethanol.

**Characterization:** Scanning electron microscopy (SEM) images were obtained using a Hitachi HR-SEM SU8000 microscope at the accelerating voltage of 5 kV. Transmission electron microscope (TEM) and high-angle annular dark-field scanning TEM (HAADF-STEM) images were taken by using a JEOL JEM-2100F microscope at the accelerating voltage of 200 kV. Small angle X-ray scattering (SAXS) profiles were recorded by a Rigaku NANO-Viewer (Cu K $\alpha$  radiation) with a camera length of 700 mm operated at 40 kV and 30 mA. Wide-angle powder X-ray diffraction (XRD) profiles were recorded with a Rigaku Rint 2500 diffractometer with monochromated Cu K $\alpha$  radiation. X-ray photoelectronic spectroscopy (XPS) spectra were recorded at room temperature by using a JPS-9010TR (JEOL) instrument with an Mg K $\alpha$  X-ray source. All binding energies were calibrated by referencing to C1s (285.0 eV). Nitrogen adsorption-desorption data was obtained with a Belsorp 28 apparatus (Bel Japan) at 77 K. UV-vis absorption spectra were recorded by a JASCO V-570 UV-vis-NIR spectrometer.

**Electrochemical analysis:** Cyclic voltammograms (CVs) and chronoamperometric curves were achieved with a CHI 842B electrochemical analyzer (CH Instrument, USA). A conventional three-electrode cell was used, including an Ag/AgCl electrode as a reference electrode, a platinum wire as a counter electrode, and a glassy carbon electrode (GCE, 3 mm in diameter) modified by catalyst as a working electrode. Prior to the surface coating, the GCE was polished carefully with 1.0 and 0.05  $\mu$ m alumina powder and rinsed with deionized water, followed by drying with nitrogen gas. After being carefully cleaned, the samples were coated on the surface of GCE at the same loading of 5.0  $\mu$ g. Then, Nafion solution (5.0  $\mu$ L, 0.1 wt%) was coated on the surface and was dried completely at room temperature. Before electrochemical experiments, we electrochemically cleaned the samples to completely remove the organic molecules. The applied condition is as follows; potential range from -0.2 to 1.5 (vs. Ag/AgCl), scan rate 500 mV·s<sup>-1</sup>, and 100 cycles. The formic acid oxidation reaction investigations were carried out in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution containing 0.5 M formic acid. All potential values were referenced to an Ag/AgCl (saturated KCl) electrode.

Fig. S1



**Fig. S1** | (Left column) SEM images and (right column) the corresponding particle size distributions of MPNs prepared under various conditions ((a) 0.00 wt% F127, (b) 0.25 wt% F127, (c) 0.50 wt% F127, (d) 1.00 wt% F127, and (e) 1.50 wt% F127).

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Fig. S2
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**Fig. S2** | Low-magnified TEM image of MPNs prepared under typical condition (1.0 wt% F127).





**Fig. S3** | N<sub>2</sub> adsorption isotherms of MPNs prepared under typical condition (1.0 wt% F127).





**Fig. S4** | Cyclic voltammograms (CVs) obtained in 0.5 M  $H_2SO_4$  solution with a scan rate of 50 mV·s<sup>-1</sup> ((Red) MPN sample and (Black) PB sample).





**Fig. S5** | ED patterns taken from one particle of MPNs prepared under typical condition (1.0 wt% F127).



**Fig. S6** | Highly magnified TEM image of one MPN particle prepared under typical condition (1.0 wt% F127).

Fig. S6

Fig. S7



**Fig. S7** | Wide-angle XRD profile of MPNs prepared under typical condition (1.0 wt% F127).





**Fig. S8** | (a) XPS survey spectrum of MPNs prepared under typical condition (1.0 wt% F127), and (b and c) XPS spectra for (b) Pd 3d and (c) N 1s peaks.



Fig. S9 | Highly-magnified SEM image of MPNs prepared without F127.

Fig. S10



**Fig. S10** | (a-b) Low- and (c) highly-magnified SEM images of Pd sample prepared without F127 and HDPC.





**Fig. S11** | (a) Photographs of various solutions ((1) Na<sub>2</sub>PdCl<sub>4</sub> solution, (2) F127+Na<sub>2</sub>PdCl<sub>4</sub> solution, (3) HDPC+Na<sub>2</sub>PdCl<sub>4</sub> solution, (4) HDPC+F127+Na<sub>2</sub>PdCl<sub>4</sub> solution, and (5-8) HDPC+F127+Na<sub>2</sub>PdCl<sub>4</sub> solutions with different Na<sub>2</sub>PdCl<sub>4</sub> concentrations (0.625 mM, 1.250 mM, 2.500 mM, and 5.000 mM, respectively). (b) UV-Vis spectra of various solutions (Solution compositions are noted inside the figure.) (c) UV-Vis spectra of HDPC+F127+Na<sub>2</sub>PdCl<sub>4</sub> solutions with different Na<sub>2</sub>PdCl<sub>4</sub> concentrations (0.625 mM, 1.250 mM, 2.500 mM, 2.500 mM, and 5.000 mM, respectively). An absorption band at 258 nm corresponds to the  $\pi$ - $\pi$ \* transition in the pyridinium group of HDPC.



**Fig. S12** | SEM images of MPNs prepared under various conditions ((a) 0.25 wt% F127, (b) 0.50 wt% F127, (c) 1.00 wt% F127, and (d) 1.50 wt% F127).

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Fig. S13
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**Fig. S13** | Highly magnified SEM image of MPNs prepared with CTAC instead of HDPC. Compared to HDPC system, the mesostructural ordering is decreased, because the self-organizing ability of CTAC would be weaker than that of HDPC. It is expected that HDPC molecules are readily self-organized due to effective  $\pi$ - $\pi$  interaction of hydrophilic parts.

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Fig. S14
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**Fig. S14** | (Left column) SEM images and (right column) the corresponding particle size distributions of MPNs prepared with CTAC under various conditions ((a) 0.00 wt% CTAC, (b) 0.25 wt% CTAC, (c) 0.50 wt% CTAC, and (d) 1.00 wt% CTAC). The average particle sizes are (a) 57 nm, (b) 48 nm, (c) 44 nm, and (d) 35 nm, respectively.





**Fig. S15** | Cyclic Voltammograms (CVs) and chronoamperometric curves for formic acid oxidation reaction catalyzed by MPNs prepared with varied F127 concentration (orange) 0.00 wt%, (blue) 0.25 wt%, (red) 1.00 wt%, (black) Pd black, and (olive) Pd nanoparticles), in 0.5 M H<sub>2</sub>SO<sub>4</sub> containing 0.5 M HCOOH. The current densities (Y-axis) are normalized by (a, c) the Pd mass (mg) and (b, d) the Pd electrochemical surface area (cm<sup>2</sup>), respectively.





**Fig. S16** | Cyclic voltammograms (CVs) for formic acid oxidation reactions catalyzed by (a) MPNs, (b) PB, and (c) Pd nanoparticles (solid line) before and (dashed line) after 3000s chronoamperometric tests. All the tests are conducted in  $0.5 \text{ M H}_2\text{SO}_4$  containing 0.5 M HCOOH. The current densities are normalized by the Pd mass (mg).