Supporting Information

Synthesis of octahedral Pt-Pd alloy nanoparticles for improved catalytic activity and stability in methanol electrooxidation

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Experimental procedure

Synthesis. The octahedral Pt-Pd alloy nanoparticles were prepared by simultaneously reducing Pd and Pt salt in aqueous solution. All chemicals used were of analytical grade. The 50 mL aqueous solution containing 269 mM glycerol ($C_3H_5(OH)_3$, Fluka) as a reducing agent was prepared in a flask. To this mixture, 2 mM H_2PtCl_6 (Fluka), 2 mM Na_2PdCl_4 (Aldrich) and 50 mg poly(vinyl pyrrolidone) (PVP, MW = 29,000, Aldrich) were dissolved with continuous stirring. The mixed solution with a brown colour was raised by 1 ^{o}C min^{-1} and was kept for 3 h at 100 ^{o}C until Pt and Pd salts were completely reduced. The resulting colloid solution was cooled at 25 ^{o}C and black colloid was observed indicating the formation of Pt-Pd alloy nanoparticles (NPs).

Preparation of carbon-supported Pt-Pd alloy catalyst. The carbon (Vulcan XC-72R) powder was stirred in 5 M HCl solution at 50 ^{o}C for 12 h and then washed with water and then with ethanol several times to remove impurity and excess HCl. An aqueous solution (10 mL) containing 1 mL of H_2SO_4 (0.5 M) and 1 mL of 1 M acetic acid was prepared in a flask. The as-synthesized Pt-Pd alloy NPs (60.2 mg) and Vulcan XC-72R (240.8 mg) treated were added to the solution and mixed with continuous stirring at 25 ^{o}C for 24 h. The resulting powders were precipitated and washed with water and ethanol several times to remove PVP as a surfactant.

Characterizations. For the structure analysis of the catalysts, X-ray diffraction (XRD) analysis was carried out using Rigaku X-ray diffractometer with Cu K$_\alpha$ (λ = 0.15418 nm) source with a Ni filter. The source was operated at 40 kV and 100 mA. The 2θ angular scan from 20° to 80° was explored at a scan rate of 5° min^{-1}. For all the XRD measurement, the resolution in the scans was kept at 0.02°. The morphology and size distribution of the catalysts were characterized by field-emission transmission electron microscopy (FE-TEM) using a Tecnai G2 F30 system operating at 300 kV. TEM samples were prepared by placing drops of catalyst suspension dispersed in ethanol on a carbon-coated copper grid. Energy dispersive X-ray (EDX) analysis of the catalysts was performed on a field emission transmission electron microscope (FE-TEM, Tecnai G2 F30 system). X-ray photoelectron spectrometry (Thermo Scientific, K-Alpha) study was carried out with the Al K$_\alpha$ X-ray source of 1486.8 eV at the chamber

pressure below 1×10^{-8} Torr and 200 W beam power. All high resolution spectra were collected using a pass energy of 46.95 eV. The step size and time per step were chosen to be 0.025 eV and 100 ms, respectively. Both ends of the baseline were set sufficiently far so as not to distort the shape of spectra, including tails. Small variation of the range of the base line did not affect the relative amount of fitted species (less than 1%). The C 1s electron binding energy was referenced at 284.6 eV and a nonlinear least-squares curve-fitting program was employed with a Gausian-Lorentzian production function.

Electrochemical properties of the catalysts were measured in a three-electrode cell at 25 ^{o}C using a potentiostat (Eco Chemie, AUTOLAB). A Pt wire and Ag/AgCl (in saturated KCl) were used as a counter and reference electrode, respectively. The glassy carbon electrode as a working electrode was polished with 1, 0.3, and 0.05 μm Al_2O_3 paste and then washed in deionized water. The catalyst ink was prepared by ultrasonically dispersing catalyst powders in an appropriate amount of Millipore water. The catalyst ink was dropped onto a glassy carbon working electrode. After drying in 50 ^{o}C oven, total loading of catalyst was 20 μg cm^{-2}. To clearly characterize electrochemical properties, electrochemical treatment was carried out between -0.2 and +1.0 V (30 CV cycles) with a scan rate of 50 mV s^{-1}. To compare electrochemical properties and catalytic activity of the catalysts, cyclic voltammograms (CVs) were obtained between -0.2 to +1.0 V in 0.1 M $HClO_4$ and 0.1 M $HClO_4$ + 2 M CH_3OH, respectively. For CO-stripping measurements the catalysts were kept at +0.2 V for 3600 sec in 0.1 M $HClO_4$ + 2 M formic acid, and then voltammetry was carried out from -0.2 to +1.0 V. For an accelerated stability test, the catalysts were kept at +0.45 V for 1 h in 0.1 M $HClO_4$ + 2 M CH_3OH and then CVs were obtained in 0.1 M $HClO_4$ + 2 M CH_3OH. The electrochemical active surface areas (EASAs) of these catalysts were determined by integrating hydrogen adsorption/desorption areas of the CVs (assuming 210 μC cm^{-2} after double layer correction).

The transition of glycerol as reducing agent was confirmed by Fourier Transform Infrared (FT-IR) Spectroscopy (Bio-Rad). The samples were prepared by reducing sodium palladium (Ⅱ) chloride (Na_2PdCl_4, Aldrich) in glycerol aqueous solution (Glycerol : H_2O = 4 : 1 v/v%) at 100 ^{o}C for 12 and 24

h, respectively. The spectra were collected within the range of 1000 and 2000 cm^{-1}. All the spectra were

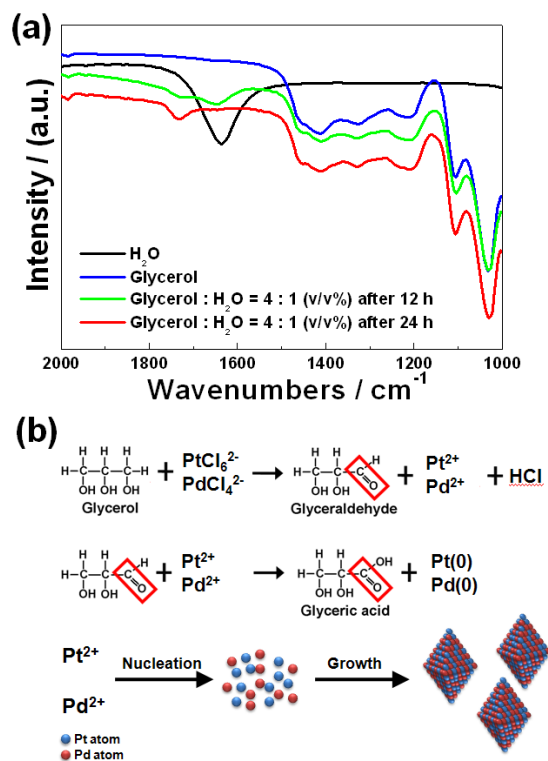recorded and plotted in the same scale on the transmittance axis.

Figure S1. (a) FT-IR spectrum with respect to the reduction of Na$_2$PdCl$_4$ with glycerol as a reducing agent in aqueous solution at 12 and 24 h in comparison with H$_2$O. (b) The formation mechanism of octahedral Pt-Pd nanoparticles synthesized using glycerol as a reducing agent.
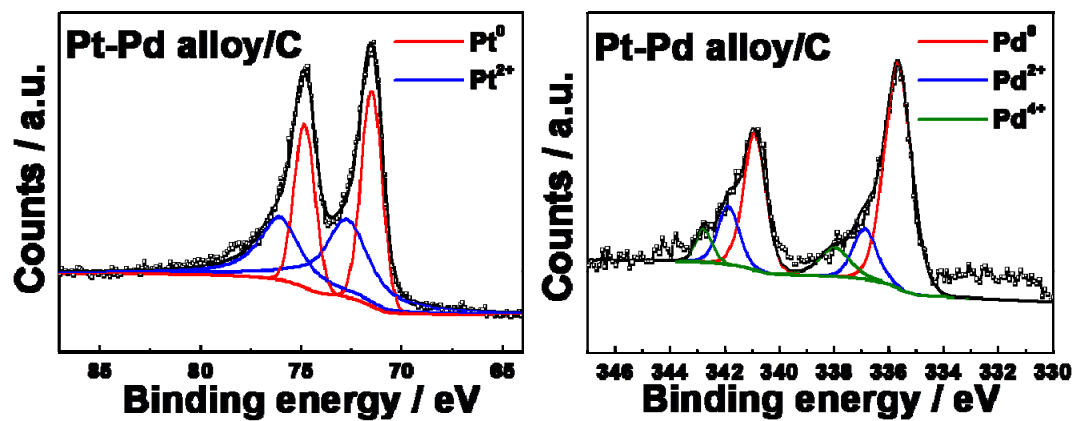
Figure S2. Pt 4f and Pd 3d XPS spectra in PtPd alloy/C for surface and chemical analysis.