Supporting Information

Reviving Galvanic Cells to Synthesize Core-Shell Nanoparticles with Quasi-Monolayer Pt Shell for Electrocatalytic Oxygen Reduction

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METHODS

Synthesis of Pd$_c$Pt$_{qms}$/C.

Pd/C powder (Ishifuku Metal Industry, 100mg) is dispersed in the N$_2$-saturated 0.01 M CuSO$_4$ and 0.5 M H$_2$SO$_4$ solution, with continual stirring. Then, a Cu wire is immersed into the above mixture. Near 20 hours later, Cu wire is extracted and successively N$_2$-saturated 10 mM K$_2$PtCl$_4$ solution is added into the suspension. After 7 minutes, the suspension is filtered and dried to obtain Pd$_c$Pt$_{qms}$/C.

Synthesis of Pd$_c$Pt$_{qms}$/C-ref.

Pd/C powder (Ishifuku Metal Industry, 20.1 mg) is ultrasonically suspended in a mixture of isopropyl alcohol (absolute, about 6 mL) and deionized water (4 mL) for 0.5 hour. Then, Pd/C ink (5 µL) is micropipetted onto a glassy carbon electrode (GCE) surface (5mm, 0.1964 cm^2) and dried at ambient temperature until a uniform thin film is formed. At last, Pd/C layer is coated by a 2.5 µL mixture of isopropyl alcohol and Nafion solution (0.36 wt %).

The underpotential deposition of Cu on Pd/C is performed using a potentiosat/galvanostat (Hokuto-denko, Japan) in a conventional three-electrode electrochemical cell, where Pt mesh, a Ag/AgCl (in 3.33 molL^{-1} KCl) electrode and a N$_2$-saturated 10 mM CuSO$_4$/0.5 M H$_2$SO$_4$ solution are used as the counter electrode, reference electrode and electrolyte. The deposition potential for Cu on Pd/C is determined by the electrodeposition curves of Cu on Pd/C (Figure 1). The electrodeposition time is about 5 minutes. The following displacement time of Cu on Pd/C in a N$_2$-saturated 10 mM K$_2$PtCl$_4$/0.5 M H$_2$SO$_4$ solution is about 7 minutes.

Electrochemical measurements.

All electrochemical measurements are performed using a potentiosat/galvanostat (Hokuto-denko, Japan) in a conventional three-electrode electrochemical cell, where Pt foil, a glassy carbon electrode (GCE, 5mm, 0.1964 cm^2) with catalyst, a relative hydrogen electrode and a 0.1 M HClO$_4$ solution are used as the counter electrode, working electrode, reference electrode and electrolyte, respectively. The temperature of electrochemical measurements is 298 K.

Cyclic voltammogram is recorded from ca. 0.1 V to 1.2 V at a scan rate of 50 mVs^{-1} in N$_2$-saturated 0.1 M HClO$_4$ solution. Electrochemical surface area is determined by integrating the hydrogen surface adsorption area in cyclic voltammogram. Linear sweep voltammogram is recorded from 0.2 to 1.2 V at a scan rate of 10 mVs^{-1} with the different rotating speed (2500, 1600, 1200, 900, 700, 500, and 300 rpm) in O$_2$-saturated 0.1 M HClO$_4$ solution. Specific activity at 0.90 vs. RHE is calculated using the koutechy-Levich plots.

Structural characterization.

ICP-AES is carried out on performed on an IRIS Intrepid II XSP from Thermo Electron Corporation. TEM and EDS are obtained on a FEI Tecnai G2 F20 S-Twin probe corrector microscope.

In-situ XAS measurements are performed at the beamline BL01B1 in SPring-8 (Japan) using a self-designed electrochemical cell powered by a

potentiosat/galvanostat (Hokuto-denko, Japan). All samples for in-situ XAS measurement have been sprayed onto carbon paper mixing with Nafion solution. The synchrotron radiation X-ray from the storage ring is monochromated by a Si (111) crystal. XAS signal at Pt-L_{III}, Pt-L_{II} and Pd K edges is measured via a fluorescence mode with 19 elements solid state detector or a transmission mode with ionic chamber, respectively. Electronic structure (Pt 5d orbital vacancy) is calculated from the XANES spectra at Pt L_{III} and Pt L_{II} edges. Local structure (Pt-Pt coordination number, Pt-Pt bond distance, Debye-Waller factor) is fitted from the EXAFS spectra at Pt L_{III} edge. The EXAFS function at Pt-L_{III} is obtained by subtracting the post-edge background from the overall absorption coefficient, and then normalizing to the edge jump. The normalized function is converted to k space, weighted by k^3 to compensate for the damping of the backscattering oscillation in the high k region. Subsequently, k^3-weighted data are converted to r-space by Fourier transformation to identify the backscattering contributions of each coordination shell. EXAFS structural analysis is performed with the REX2000 data analysis software. Based on the referenced structural model of monolayer Pt on Pd (111) facet, all fitting are performed by the FEFF8 code.
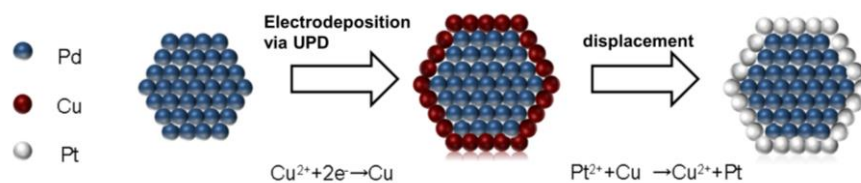
Figure S1. Adzic's method for synthesizing Pd_cPt_{qms}/C-ref.

The detail of Adzic's method has described in experimental section. In brief, it contains the underpotential deposition (UPD) of Cu on Pd and successively the displacement of Cu by Pt.
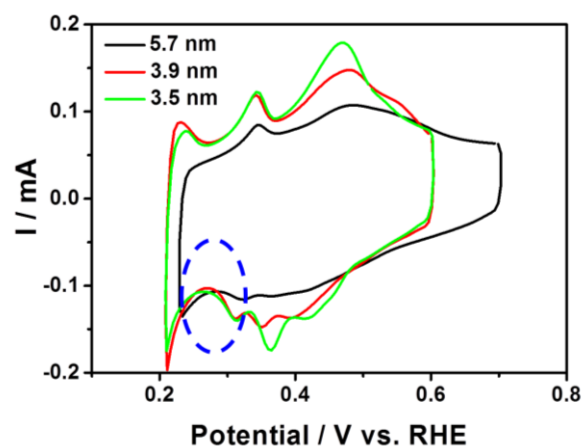
Figure S2. Cu UPD potentials on different Pd materials.

Differing with Cu UPD on Pd single crystal, the potential of Cu UPD on Pd NPs is dependent on the properties of Pd NPs, such as particle size, surface structure, and so on.
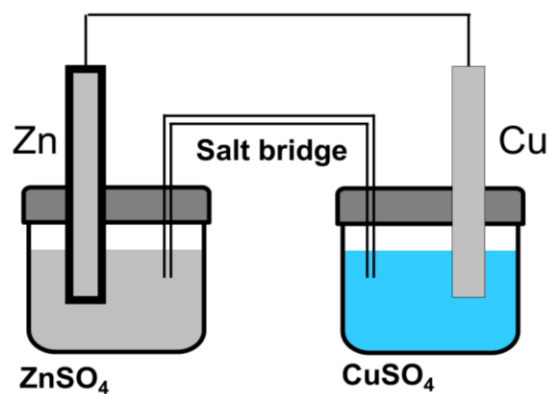
(-) Zn (s)|Zn^{2+} (c1) || Cu^{2+} (c2)|Cu (s) (+)

Figure S3. Typical Zn-Cu galvanic cell (anode reaction: Zn = Zn^{2+} + 2e; cathode reaction: Cu^{2+} + 2e = Cu), while the dissolution of Zn to Zn^{2+} induces the deposition of Cu^{2+} to Cu.
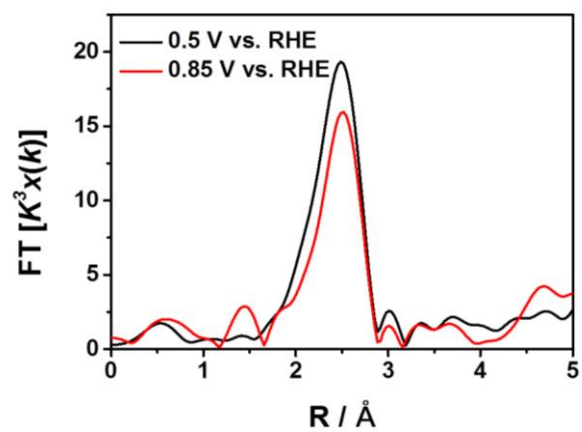
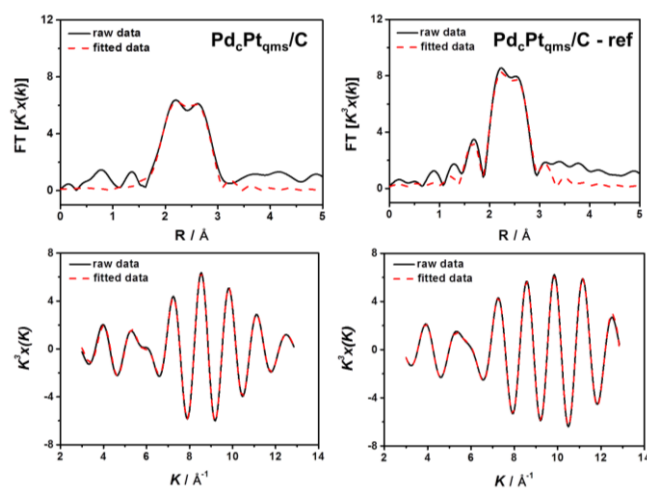**Figure S4.** Structural changes of pure Pd_c at different potentials.

Figure S5. EXAFS Fitting of in-situ XAS (0.5 V vs. RHE) at Pt L_{III} edges of Pd_cPt_{qms}/C from our proposed method and Pd_cPt_{qms}/C-ref from the traditional one.
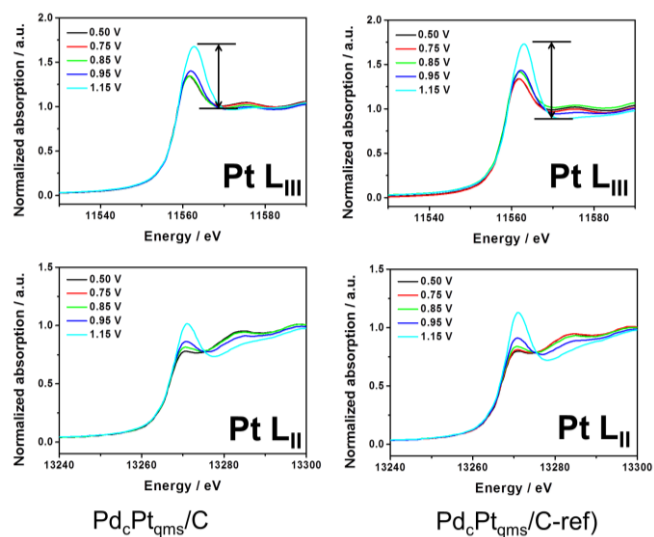
Figure S6. XANES spectra of in-situ XAS (0.5, 0.75, 0.85, 0.95, 1.15 V vs. RHE) at Pt L_{III} and L_{II} edges of Pd_cPt_{qms}/C from our proposed method and Pd_cPt_{qms}/C-ref from the traditional one.
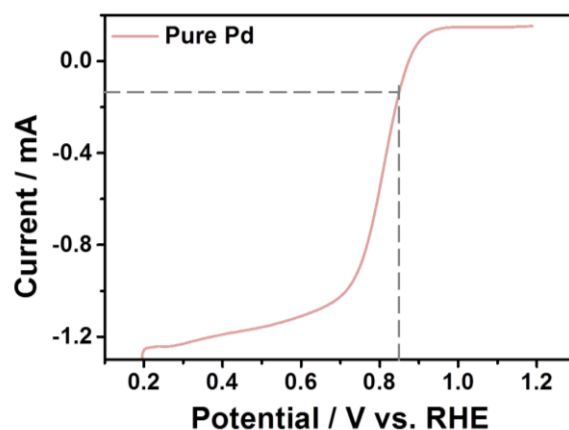
Figure S7. LSV (10 mV/s, 1600 rpm) of pure Pd_c in 0.1 M O_2-saturated $HClO_4$.

Pd is active toward oxygen reduction at low potential. With the increase of potential, Pd will adsorb oxygenated species, thus generate a slope at the diffusion-limiting current, which is an important character to detect the exposure of Pd_c in Pd_cPt_{qms}/C.
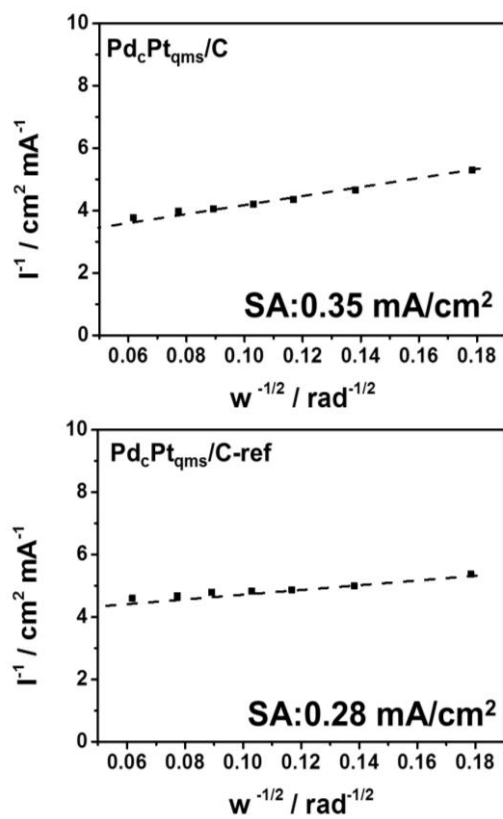
Figure S8. Koutecky-Levich plots of Pd_cPt_{qms}/C from our proposed method and Pd_cPt_{qms}/C-ref from the traditional one.