Supporting information

Stability Issues in Pd-based Catalysts: The Role of Surface Pt in Improving the Stability and Oxygen Reduction Reaction (ORR) Activity

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Synthesis of Pd nanoparticles (control-experiment)

We synthesized Pd nanoparticles (without hydrogen) using L-ascorbic acid as a reducing agent, *i.e.*, Pd seed prepared without hydrogen-containing reducing agent such as $NaBH_4$. For a typical synthesis of Pd (without hydrogen), L-ascorbic acid (60 mg) was dissolved in water and it was heated to 80°C. Meanwhile, an aqueous solution of Pd^{2+} (57 mg K_2PdCl_4 in 3 ml water) was added drop-wise to the above solution. Then the mixture was heated for 3 h at ~80°C. The as-prepared Pd nanoparticles were supported on carbon (Vulcan XC-72) to get 20 wt% precious metal loading on the carbon-support. The carbon-supported Pd nanoparticles synthesized as-mentioned above was treated with 0.1 mM K_2PtCl_4 (Pt^{2+}) solution to deposit Pt on the surface of Pd (*i.e.*, Pt/Pd (without hydrogen)). The Pt/Pd catalyst was synthesized following the Cu deposition method reported in the literature.[13]

Figs. S1 and **S2** show the cyclic voltammograms (CVs) and oxygen reduction reaction (ORR) voltammograms of carbon-supported Pd (without hydrogen), Pt/Pd (without hydrogen), and Pt/Pd (synthesized by Cu deposition) in 0.1 M $HClO_4$ solution. The Pt/Pd (without hydrogen) shows features similar to that of Pd (without hydrogen) and their ORR voltammograms are almost comparable. On the other hand, synthesis of Pt/Pd by Cu deposition results in a better coverage of Pt on Pd. The CV features of Pt/Pd (synthesized by Cu deposition) are similar to that of Pt and the half-wave potential of ORR is shifted positively by ~85 mV when compared to that of Pd (without hydrogen); ORR voltammogram of Pt/Pd (synthesized by Cu deposition) almost overlaps with that of standard Pt. These observations suggest that Pt-deposition is not happening on Pd (without hydrogen) surface by the galvanic displacement of Pd by Pt. This may be due to the negligible difference in their redox potentials ($PdCl_4^{2-}$/Pd (0.591 *vs.* reversible hydrogen electrode (RHE)) and $PtCl_4^{2-}$/Pt (0.775 *vs.* RHE)). The surface hydrogen atoms or Cu atoms on Pd-H and Pd-Cu, respectively, play an important role in reducing Pt^{2+} ions and in depositing Pt on Pd.

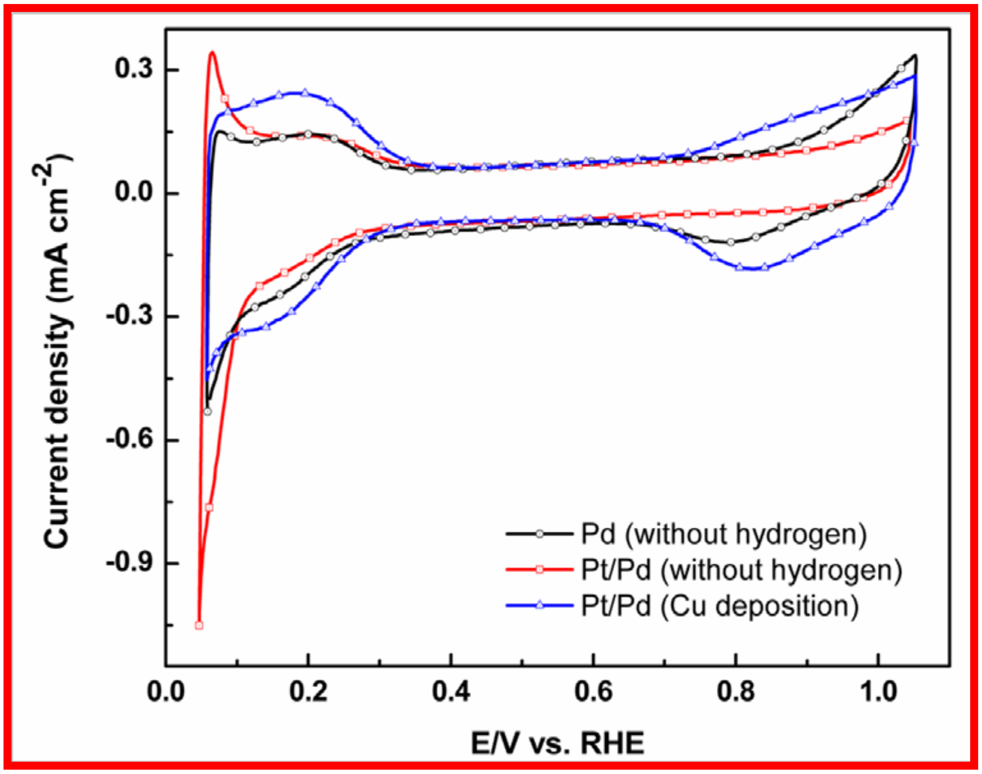

Fig. S1 Cyclic voltammograms (CVs) of Pd (without hydrogen), Pt/Pd (without hydrogen), and Pt/Pd (synthesized by Cu deposition) catalysts recorded in argon-saturated 0.1 M $HClO_4$ solution at a scan rate of 20 mV s^{-1}.

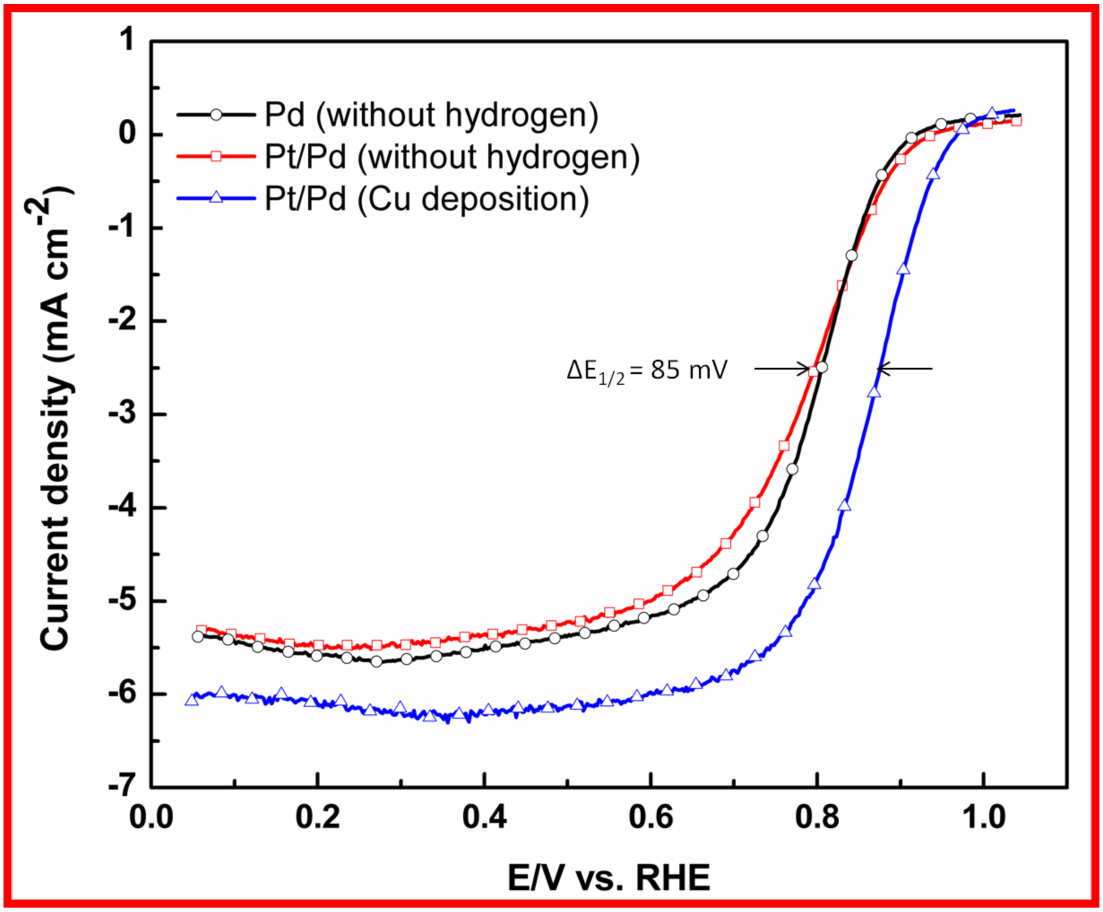

Fig. S2 Oxygen reduction voltammograms of Pd (without hydrogen), Pt/Pd (without hydrogen), and Pt/Pd (synthesized by Cu deposition) catalysts recorded in oxygen-saturated 0.1 M $HClO_4$ with 1600 rpm at a scan rate of 20 mV s^{-1}.

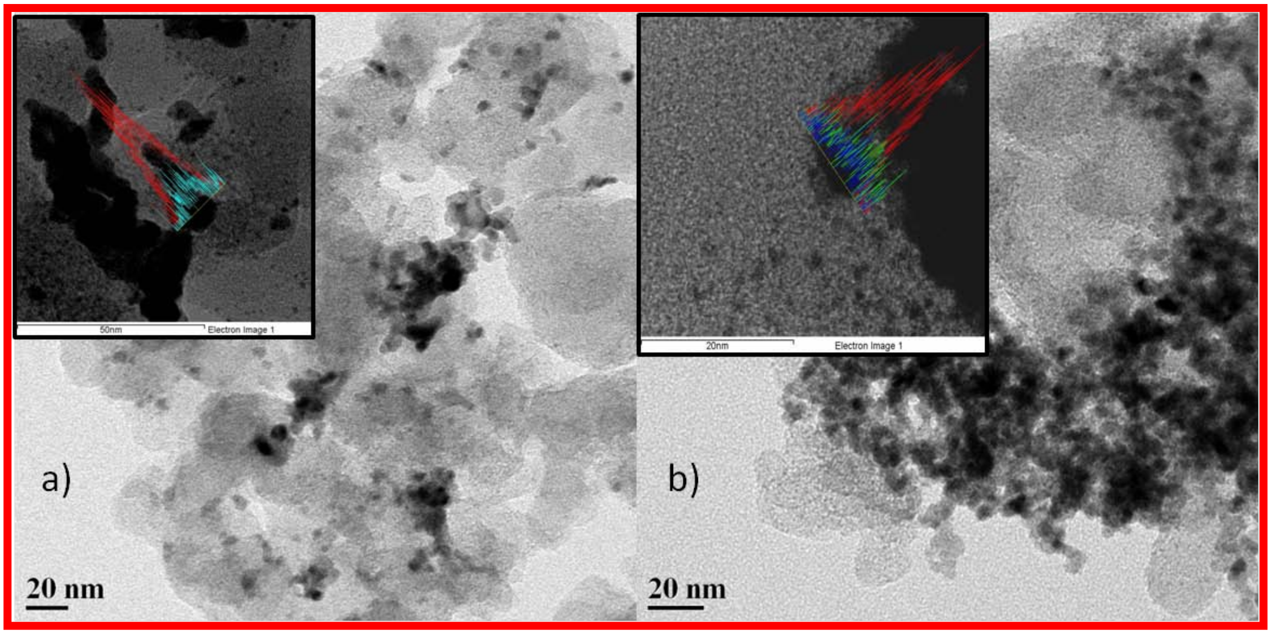

Fig. S3 TEM images of (a) Pt/Pd and (b) Pt/Pd_3Co. Inset to Figs. S3a and S3b shows EDS line scan of Pt/Pd (Pd (red) and Pt (cyan)) and Pt/Pd_3Co (Pd (red), Pt (green), and Co (blue)), respectively.

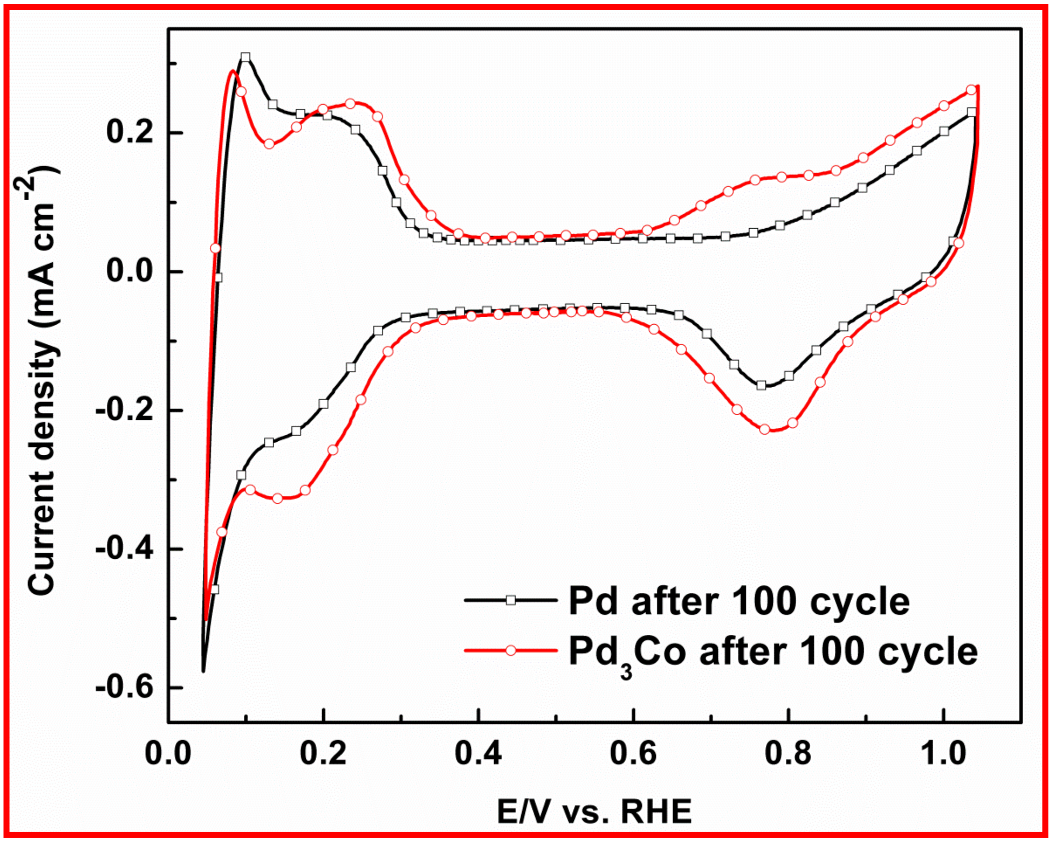

Fig. S4 Cyclic voltammograms of Pd and Pd_3Co catalysts after 100 cycles recorded in argon-saturated 0.1 M $HClO_4$ solution at a scan rate of 20 mV s^{-1}.

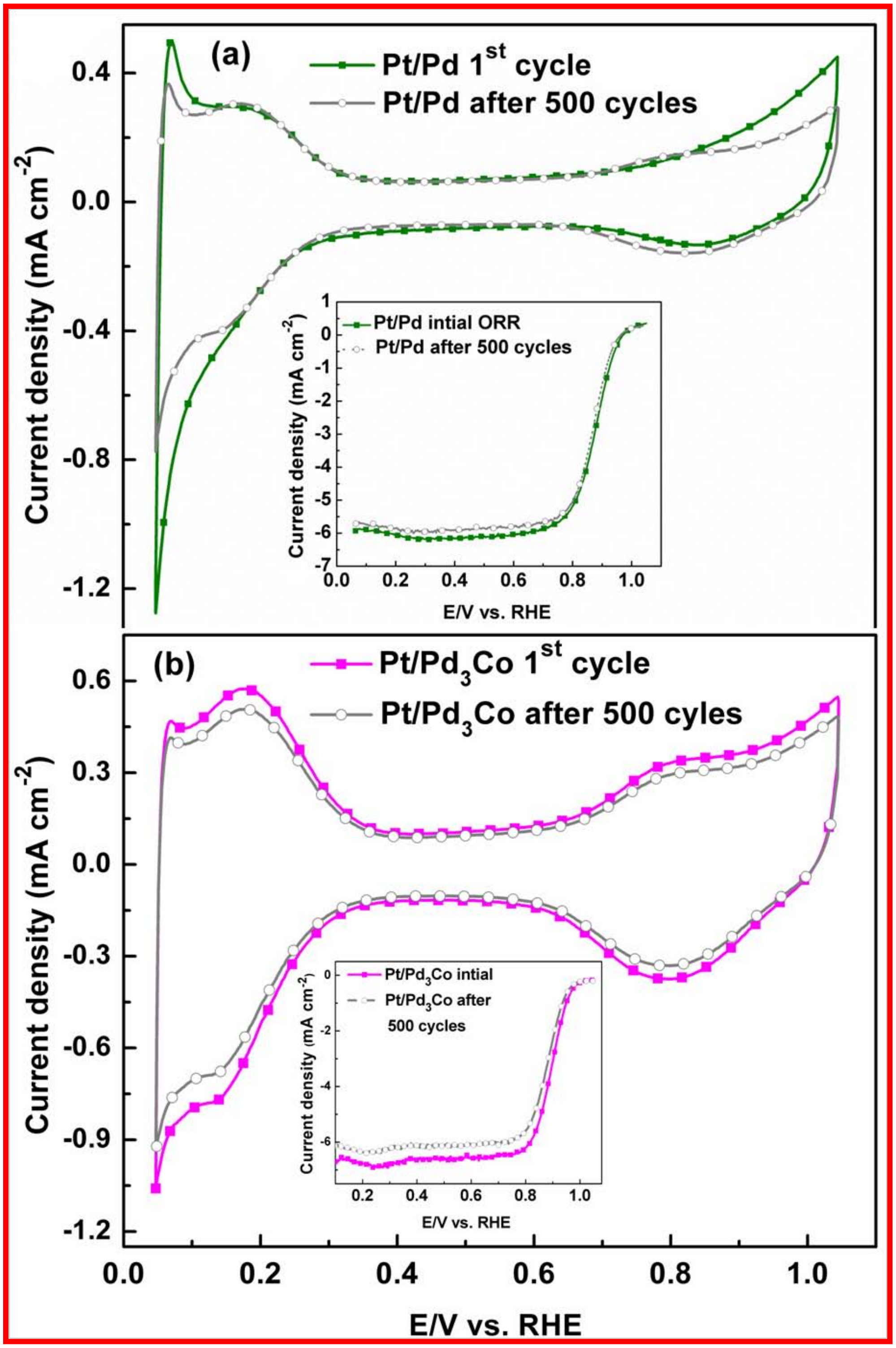

Fig. S5 Cyclic voltammograms of (a) Pt/Pd and (b) Pt/Pd_3Co (initial and after 500 cycles) recorded in argon-saturated 0.1 M $HClO_4$ solution. Insets to Fig. S5a and S5b show the ORR voltammograms of Pt/Pd and Pt/Pd_3Co catalysts, respectively.

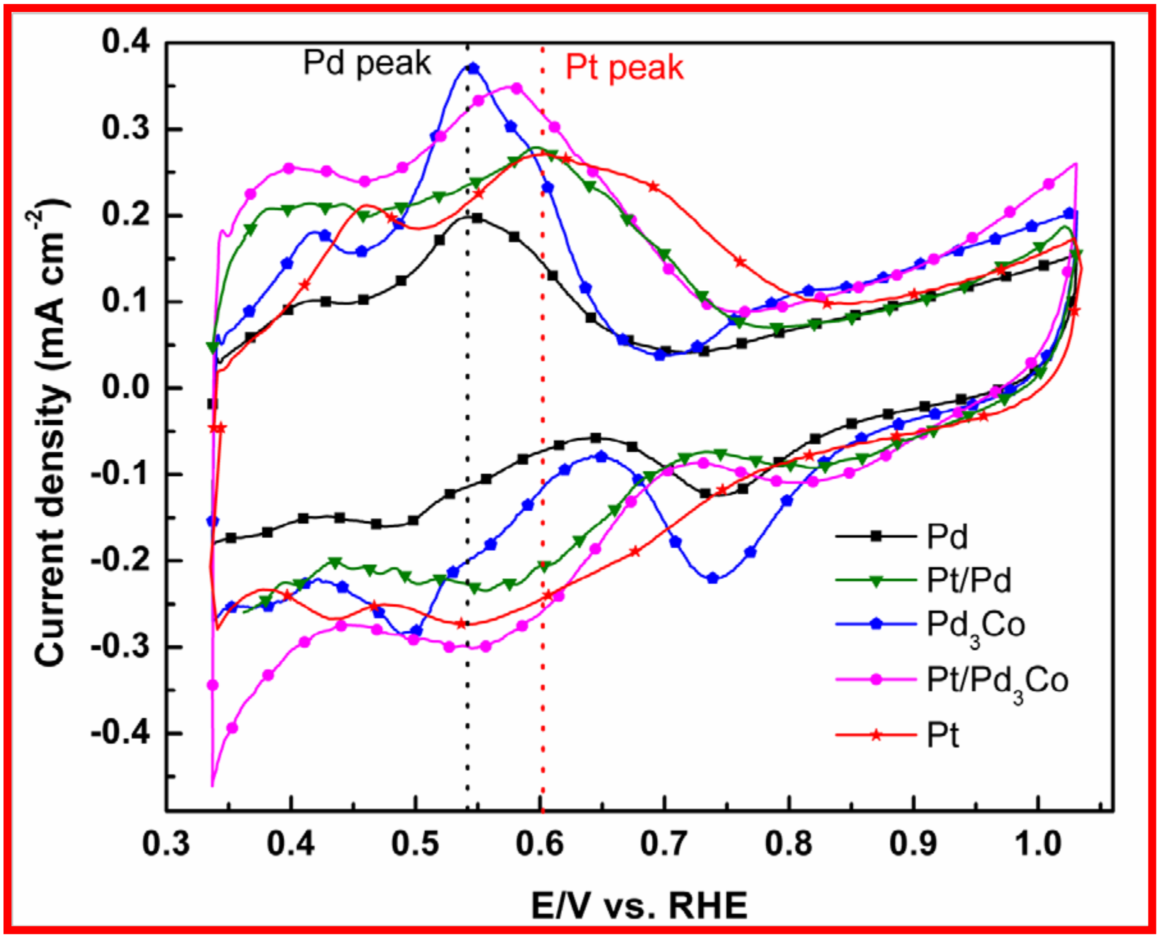

Fig. S6 Cu stripping voltammograms of Pt, Pd, Pt/Pd, Pd_3Co, and Pt/Pd_3Co recorded in argon-saturated 12 mM $CuSO_4$ solution (0.1 M $HClO_4$ as a supporting electrolyte) at a scan rate of 10 mV s^{-1}. The dotted black and red lines represent the peak positions of Pd and Pt, respectively.

Table S1 Inter-planar spacing (d_{111}) of Pd, Pd_3Co, Pt/Pd, and Pt/Pd_3Co catalysts calculated from the X-ray diffraction (XRD) patterns.

Catalyst	**d_{111} (nm)**
Pd	0.2257
Pd_3Co	0.2280
Pt/Pd	0.2255
Pt/Pd_3Co	0.2274

Table S2 Particle size of Pd, Pd_3Co, Pt/Pd, and Pt/Pd_3Co catalysts estimated from the {220} reflection of the X-ray diffraction pattern and from TEM.

Catalyst	**XRD (nm)**	**TEM (nm)**
Pd	5	~5
Pd_3Co	3	~3
Pt/Pd	5	~5
Pt/Pd_3Co	3	~3

Table S3a EDS analysis of Pt/Pd_3Co catalyst.

Element	**Atomic %**
Co	22
Pd	67
Pt	11

Table S3b EDS analysis of Pt/Pd catalyst.

Element	**Atomic %**
Pd	86
Pt	14

Table S4 Dispersion of Pd estimated using hard sphere model for different particle sizes.

Particle size (nm)	Total atoms	Surface atoms	Dispersion (%)
2.3	440	284	64
3	965	478	49
4	2287	852	37
5.25	5173	1468	28
6	7722	1916	24
10	35751	5324	15
15	120662	11988	10
20	286014	21312	7.5

Calculation of Pt:Pd ratio from dispersion (Table S4) and H_{des} charge

For Pd_3Co

Pd_3Co loading on 0.196 cm^2 of the disk electrode = 3 μg (or 15 μg cm^{-2} of 20 wt% Pd_3Co/C)

Pd loading on the disk electrode =2.53 μg (Pd:Co is 3:1 molar ratio)

The moles of Pd atoms in 2.53 μg of the catalyst = $\frac{2.53\times10^{-6}\text{g}}{106.42\text{ g/mole}} = 2.37 \times 10^{-8}$mole

The total number of Pd atoms = 2.37×10^{-8}(mole) × 6.023×10^{23} (atoms/mole) = 14.2×10^{15}

Dispersion using hard sphere model with 3 nm particle size = 0.49

The total number of surface Pd atoms with 3 nm particle size = $14.2 \times10^{15} \times 0.49 = 6.95 \times10^{15}$

So, the Pd (surface) : Pd (bulk) = 6.95×10^{15} : 14.2×10^{15} = 1:2.04

1:2.04 (Pt:Pd) is maximum ratio possible (with Pd_3Co) if all the surface Pd atoms are metallic with 3 nm particle size. *This assumes Pt is deposited on all Pd surface atoms*.

Thus, 1:4.08 is Pt:Pd ratio possible for half-a-monolayer coverage of Pt on Pd (with Pd_3Co).

H_{des} charge (after correcting for double layer and bulk hydrogen evolution) = 0.650 mC

Number of active Pd sites on Pd_3Co/C = 0.650 mC/1.6×10^{-19} = 4.06×10^{15} Pd atoms (electronic charge in Coulomb =1.6×10^{-19} C)

From the H_{upd} charge the number of surface Pd atoms = 4.06×10^{15} Pd atoms.

Number of Pt^{2+} that can be reduced with Pd-H (surface) = ($4.06 \times 10^{15}/2$) atoms

= 2.03×10^{15} (since two Pd-H is required to reduce one Pt^{2+}).

So, the ratio of Pt:Pd with Pd_3Co = (2.03×10^{15})/(14.2×10^{15}) = ~ 1:6.99

The above ratio is close to the composition obtained from EDS, ICP, and EDS line scan ~1:6 (in Pd_3Co). But, we get 1:4.08 from geometric considerations (hard sphere model), since it considers all Pd as metallic.

But, only 65% of the surface Pd is metallic (from XPS), and if we correct theoretical value (1:4.06) calculated from geometric considerations (with 0.65) (*i.e.*, 1×0.65:4.08 = 1:6.27). This is almost close to Pt:Pd obtained from H_{des} (1:6.99).

<u>For Pd</u>

The atomic weight of Pd =106.42 g/mole.

The moles of Pd atoms in 3 μg of the catalyst = $\frac{3\times10^{-6}\text{g}}{106.42\text{ g/mole}} = 2.81 \times 10^{-8}$ mole

The total number of Pd atoms 2.81×10^{-8} mole × 6.023×10^{23} = 16.92×10^{15}

Dispersion using hard sphere model with 4 nm particle size = 0.37

Number of surface atoms for a 4 nm particle = $16.92 \times 10^{15}\times0.37 = 6.26 \times 10^{15}$

So, the Pd (surface) : Pd (bulk) = 6.26×10^{15} :16.92×10^{15} = 1:2.70

<u>1:2.70 (Pt:Pd) is the maximum ratio possible (with Pd) if all the surface Pd atoms are metallic with 4 nm particle size</u>. <u>This assumes Pt is deposited on all Pd surface atoms</u>.

<u>Thus, 1:5.40 is Pt:Pd ratio possible for half-a-monolayer coverage of Pt on Pd (with Pd).</u>

H_{des} charge (after correcting for double layer and bulk hydrogen evolution) = 0.310 mC

Number of active Pd sites on Pd = 0.310 mC/1.6×10^{-19} (electronic charge in Coulomb)

$= 1.937\times10^{15}$ Pd atoms

Number of Pt^{2+} that can be reduced with Pd-H (surface) = $(1.937 \times 10^{15}/2)$ atoms (since two Pd-H is required to reduce one Pt^{2+}) = 0.968×10^{15}.

So, the ratio of Pt:Pd with Pd = $(0.968\times10^{15})/(16.92\times10^{15})$ = ~1:17.47

Pt:Pd ratio of 1:17.47 obtained from H_{upd} charge is significantly lower than the experimental composition (1:7 obtained from EDS, ICP, and EDS line scan).

In Pd case, the Pt:Pd ratio calculated from the geometric considerations (hard sphere model) is 1:5.40, since it considers all Pd as metallic.

Thus, the number of active Pd surface atoms estimated from the H_{des} charge is an underestimation because Pd is oxidizing in the H_{upd} region itself.

If we presume ~50 % Pd is oxidizing in the H_{upd} region itself (Pd_3Co:Pd ESA ratio is 2:1), and if we correct Pt:Pd ratio obtained from H_{des} for this, (i.e., 1/0.5:17.47), then the Pt:Pd ratio is 1:8.73.

But, only 65% of the surface Pd is metallic (from XPS), and if we correct theoretical value (1:5.40) calculated from geometric considerations (with 0.65) (*i.e.*, 1×0.65:5.40 = 1:8.30). This is almost close to Pt:Pd ratio obtained from H_{des} (1:8.73).

Table S5a Summary of the fitting results for the Pd 3d XPS spectra of Pt/Pd and Pt/Pd_3Co.

Sample	Species	Binding Energy (eV)	Relative Intensity (%)
Pt/Pd	Pd^0 (metallic)	335.31	66
	Pd^{2+} (PdO)	336.20	34
Pt/Pd_3Co	Pd^0 (metallic)	335.24	64
	Pd^{2+} (PdO)	335.92	36

Table S5b Summary of the fitting results for the Pt 4f XPS spectra of Pt/Pd and Pt/Pd_3Co.

Sample	Species	Binding Energy (eV)	Relative Intensity (%)
Pt/Pd	Pt^0 (metallic)	71.25	65
	Pt^{2+} (PtO)	72.47	21
	Pt^{4+} (PtO_2)	74.01	14
Pt/Pd_3Co	Pt^0 (metallic)	71.29	63
	Pt^{2+} (PtO)	72.30	22
	Pt^{4+} (PtO_2)	73.75	15