

# Supporting Information for Publication

## Trapping of Mobile Pt Species by PdO Nanoparticles under Oxidizing Conditions

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## **Sample Preparation**

The TEM grids were custom-made using a design developed in previous work.<sup>1</sup> They have a  $100\ \mu\text{m} \times 100\ \mu\text{m}$  silicon nitride membrane window with a thickness of 15 nm. The top and bottom 3 nm have been transformed into a surface oxide layer through calcination in air at 750 °C for 24 hours. High purity metals (99.999%) of both platinum and palladium used to fabricate these samples were purchased from Materion Corporation. The metals were deposited directly onto the  $2\ \text{mm} \times 2\ \text{mm}$  SiO<sub>2</sub> TEM grid surface using 10 kV Temescal electron beam evaporator. This high vacuum cryo-pumped system was pumped to a base pressure of  $1 \times 10^{-7}$  Torr prior to deposition. The film thickness was controlled by a quartz crystal microbalance (QCM), while the deposition rate was controlled to 0.03 Å/s. This system as configured is capable of controlling the film thickness to 0.1 Å. These noble metals are non-wetting on oxide surfaces so a continuous film is not formed during deposition at these very low loadings. All films were deposited to a thickness equivalent to 5 Å. Sample aging in flowing air (Albuquerque pressure = 85 kPa) was performed in a custom built heating reactor furnace<sup>2</sup> (Sabre Tube, Absolute Nano) which is equipped with a silicon wafer resistive heating element and a thermocouple. Samples were placed on top of the silicon heating element near the thermocouple to ensure they were aged at accurate temperatures.

## **Sample Characterization**

### *Transmission Electron Microscopy and Single Particle Energy-Dispersive X-ray Spectroscopy*

Transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) were used for imaging the samples before and after aging under oxidizing conditions. A JEOL 2010F 200 kV FASTEM FEG (field emission gun) TEM/STEM was used to acquire all STEM images. This microscope has a point-to-point resolution of 0.194 nm and a minimum spot size in STEM mode of 0.14 nm. It has a GATAN GIF 2000 Energy Filter, JEOL bright and dark field STEM detectors, GATAN bright and dark field STEM detectors, and an Oxford Instruments ISIS/INCA energy dispersive X-ray spectroscopy (EDS) system with an Oxford Pentafet Ultrathin Window (UTW) detector. Particle counting was performed using Digital Micrograph and EDS was analyzed using the Oxford INCA software.

### *X-ray Photoelectron Spectroscopy*

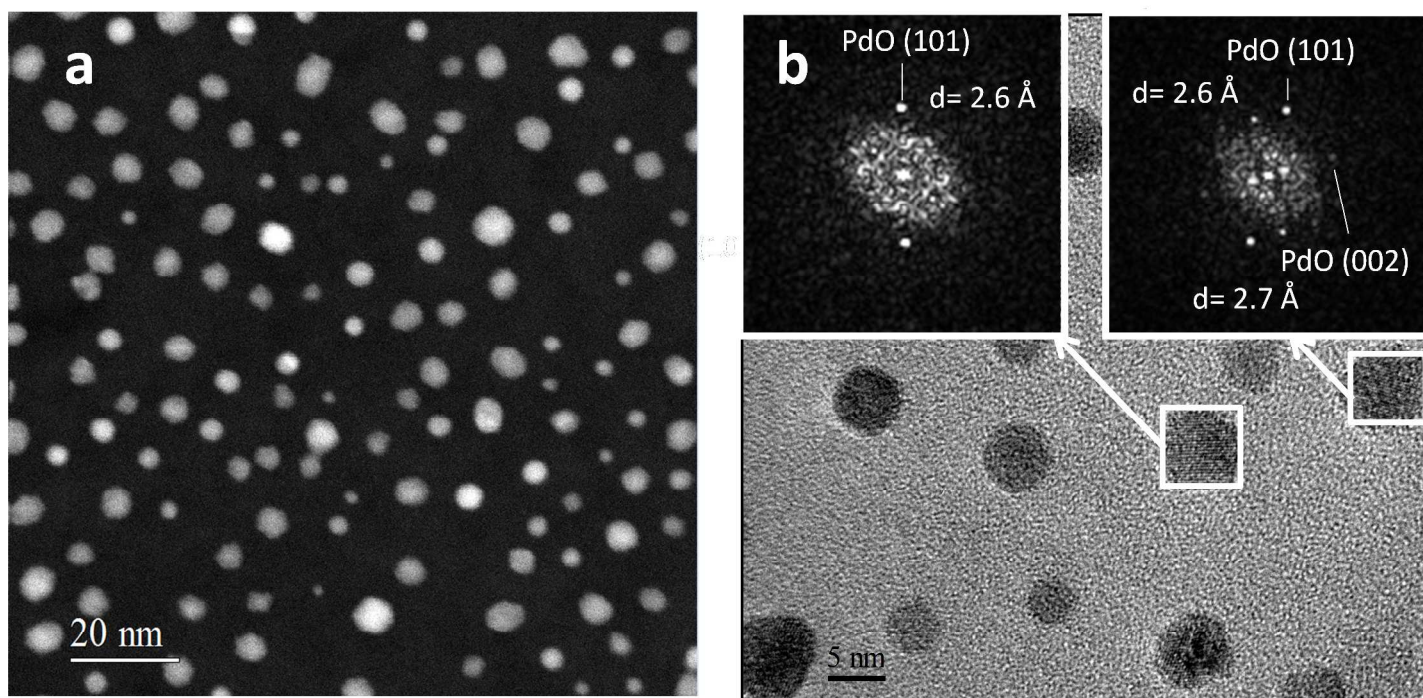
X-ray photoelectron spectroscopy (XPS) was performed using a Kratos Axis Ultra photoelectron spectrometer equipped with a monochromatic Al K $\alpha$  source operating at 300 W. The base pressure was  $2.7 \times 10^{-8}$  Pa, and operating pressure was  $2.7 \times 10^{-7}$  Pa. XPS was performed in order to study the oxidation state of Pt+PdO before and after aging in air. Analysis of the XPS spectra was performed using CASAXPS software.

### *Thermogravimetric Analysis*

Thermogravimetric analysis (TGA) was performed using a TA Instruments SDT Q600 TGA/DSC that can heat at temperatures ranging from 25 °C to 1500 °C. TGA was used to determine decomposition temperatures of bulk PdO and Pt+PdO in flowing air at Albuquerque oxygen pressures of 17.8 kPa.

## HRTEM for PdO

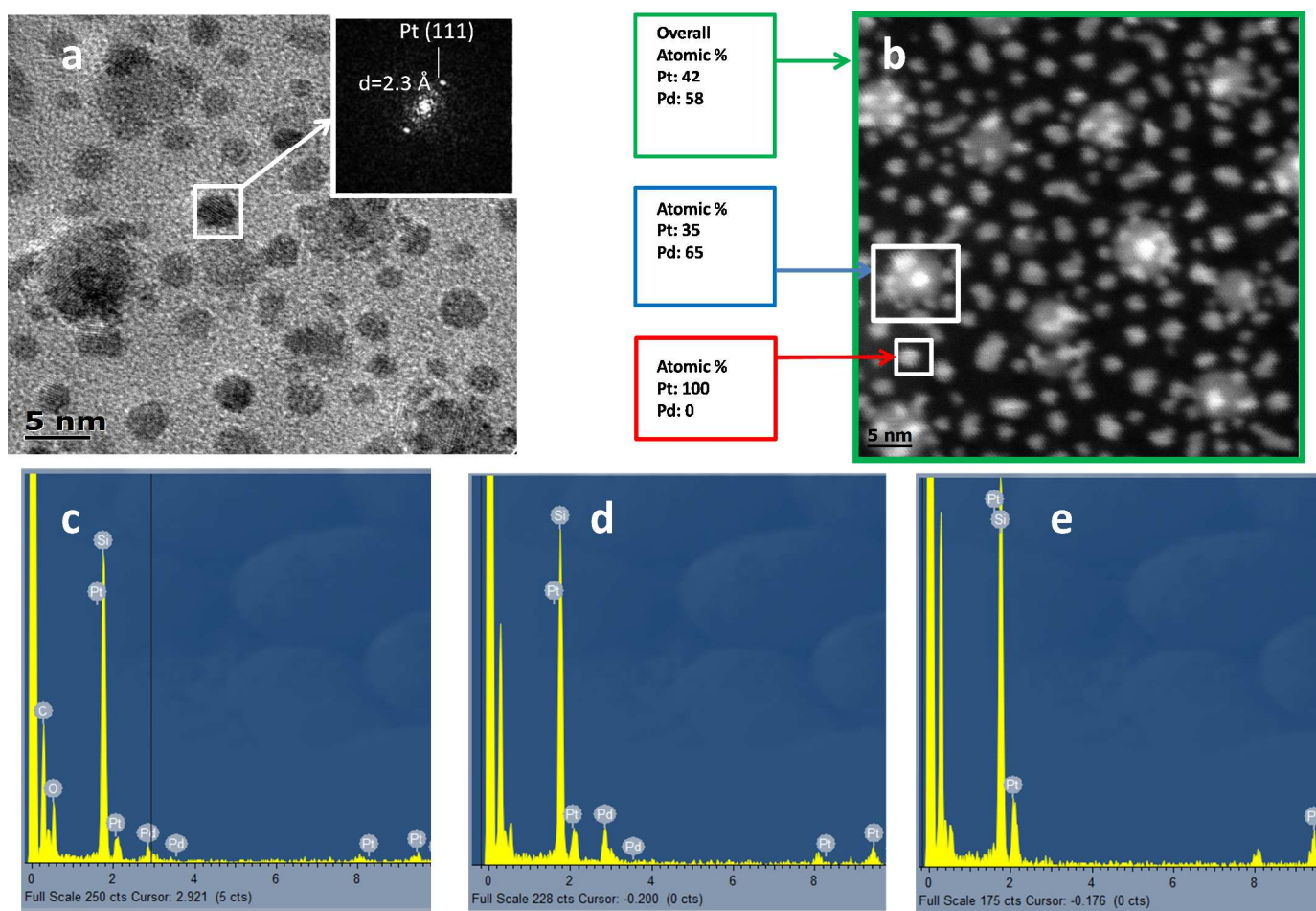
5 Å of Pd were deposited onto the model TEM grid and aged in air at 600 °C for two minutes. High resolution transmission electron microscopy (HRTEM) was used to determine the phase of the Pd nanoparticles after aging. The FFTs were obtained in Digital Micrograph showing lattice spacings of 2.6 Å and 2.7 Å corresponding to the (101) and (002) planes of PdO, respectively (Figure S1).



**Figure S1.** (a) High angle annular dark-field (HAADF)-STEM image of Pd/SiO<sub>2</sub> nanoparticles after aging in air at 600 °C for two minutes (b) HRTEM image with FFT patterns showing lattice spacings of 2.6 Å and 2.7 Å corresponding to the (101) and (002) PdO lattice planes, respectively.

## HRTEM and Single Particle EDS for Pt+PdO as prepared

Co-existing Pt+PdO nanoparticles were created by depositing 5 Å of Pt onto the PdO prepared previously (Figure S1). HRTEM and single particle EDS were used to distinguish between the PdO and Pt particles after the Pt deposition. HRTEM showed that the small particles surrounding the larger particles were Pt(111) (Figure S2a). Figure S2b shows the regions of interest in which we performed single particle EDS. The whole region shown in the HAADF-STEM image gave a 42:58 Pt:Pd atomic ratio, whereas the region containing the large particle with small particles on top gave a 35:65 Pt:Pd atomic ratio. Single particle EDS on the small particles revealed they were 100% Pt. Figure S2c-e are the EDS spectra for the overall, large particle, and small particle, respectively.



**Figure S2.** (a) HRTEM image with FFT pattern showing lattice spacing of 2.3 Å corresponding to the (111) planes of Pt (b) HAADF-STEM image with results of single particle EDS confirming that the small particles are Pt and the larger particles show some Pt and Pd because of the presence of small Pt particles that are on top of the PdO (c) Single particle EDS spectrum for the overall region in the HAADF-STEM image (Figure S2b) (d) Single particle EDS spectrum for the large particle inside the blue box in Figure S2b with a 35:65 Pt:Pd atomic ratio (e) Single particle EDS spectrum for the small particle in Figure 2c showing 100 % Pt.

### **XPS for Pt+PdO aged in air**

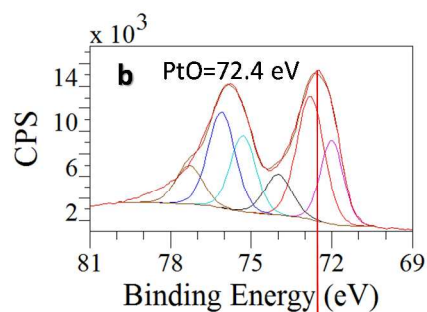
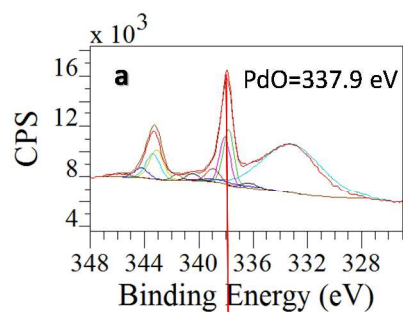
XPS was used to study the initial oxidation state of our samples and after aging in air at 650 °C for a total of 20 minutes. The oxidation state was studied after each aging time of 2,4,10 and 20 minutes. Figure S3 shows the XPS spectra for the Pd 3d and Pt 4f regions of sample 2 after the previously mentioned aging times. The as prepared Pt+PdO sample had an initial PdO peak centered at 337.9 eV (Figure S3a) and shifted to a lower binding energy of 336.8 eV after only two minutes of aging (Figure S3b) showing PdO had begun to reduce to metallic Pd in the presence of Pt and thus, forming the bimetallic Pt-Pd. After a total aging of 10 minutes it remained at a constant energy of 335.8 eV.

**Aging Time**

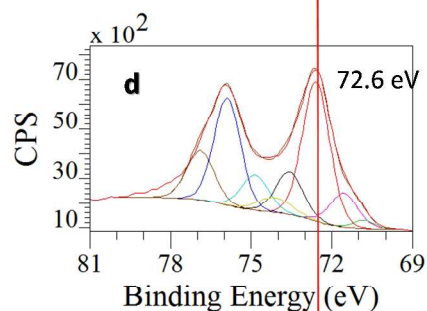
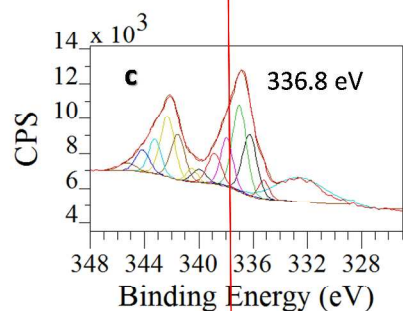
**Pd 3d**

**Pt 4f**

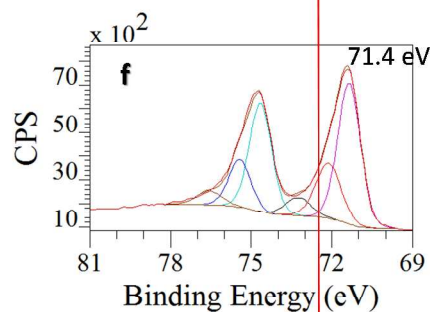
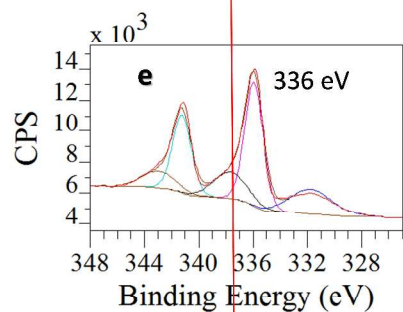
**0 minutes**



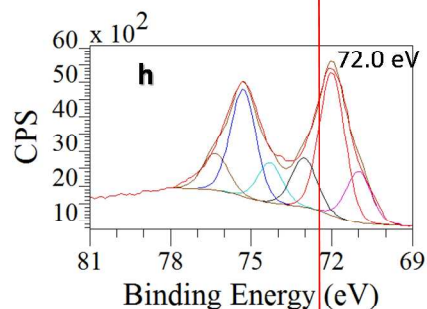
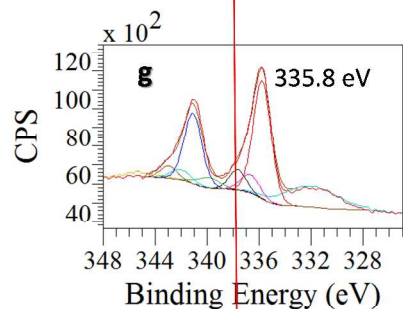
**2 minutes**



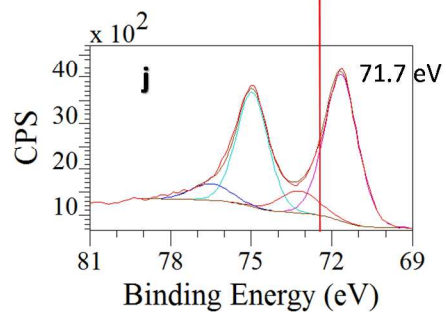
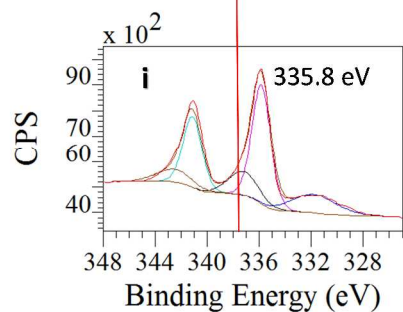
**4 minutes**



**10 minutes**



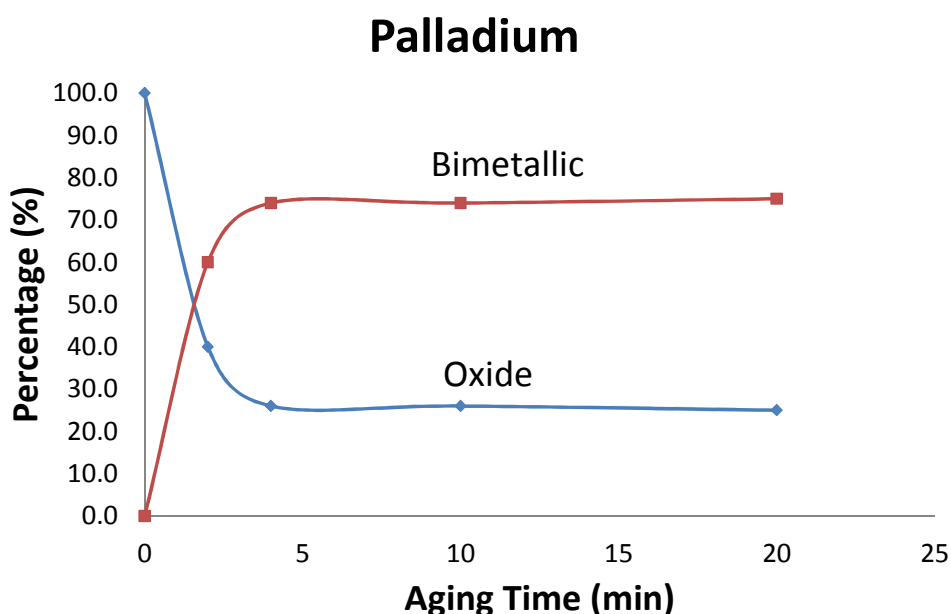
**20 minutes**





**Figure S3.** XPS spectra for Pt+PdO Sample 2 after various aging times in air at 650 °C **(a)** As prepared Pt+PdO Pd 3d region with a PdO peak at 337.9 eV **(b)** Corresponding Pt 4f region for as prepared Pt+PdO: PtO = 72.4 eV **(c)** Pd 3d region for Pt+PdO after aging for two minutes: PdO = 336.8 eV **(d)** Corresponding Pt 4f region after aging for two minutes: PtO = 72.6 eV **(e)** Pd 3d region after aging for four minutes: PdO = 336 eV **(f)** Corresponding Pt 4f region after aging for four minutes: PtO = 71.4 eV **(g)** Pd 3d region after aging for 10 minutes: PdO = 335.8 eV **(h)** Corresponding Pt 4f region after aging for 10 minutes: PtO = 72.0 eV **(i)** Pd 3d region after aging for 20 minutes: PdO = 335.8 eV **(j)** Corresponding Pt 4f region after aging for 20 minutes: PtO = 71.7 eV

Figure S4 summarizes the percentage of metal and oxide for Pd in sample 2 at the various aging time steps. We can see that the bimetallic Pt-Pd content reached a maximum of ~74% after only 4 minutes of aging. The residual oxide (26%) arises from surface oxide caused by air exposure, and it is consistent with the ~20 dispersion of these samples (average particle diameter (~4.7nm)).

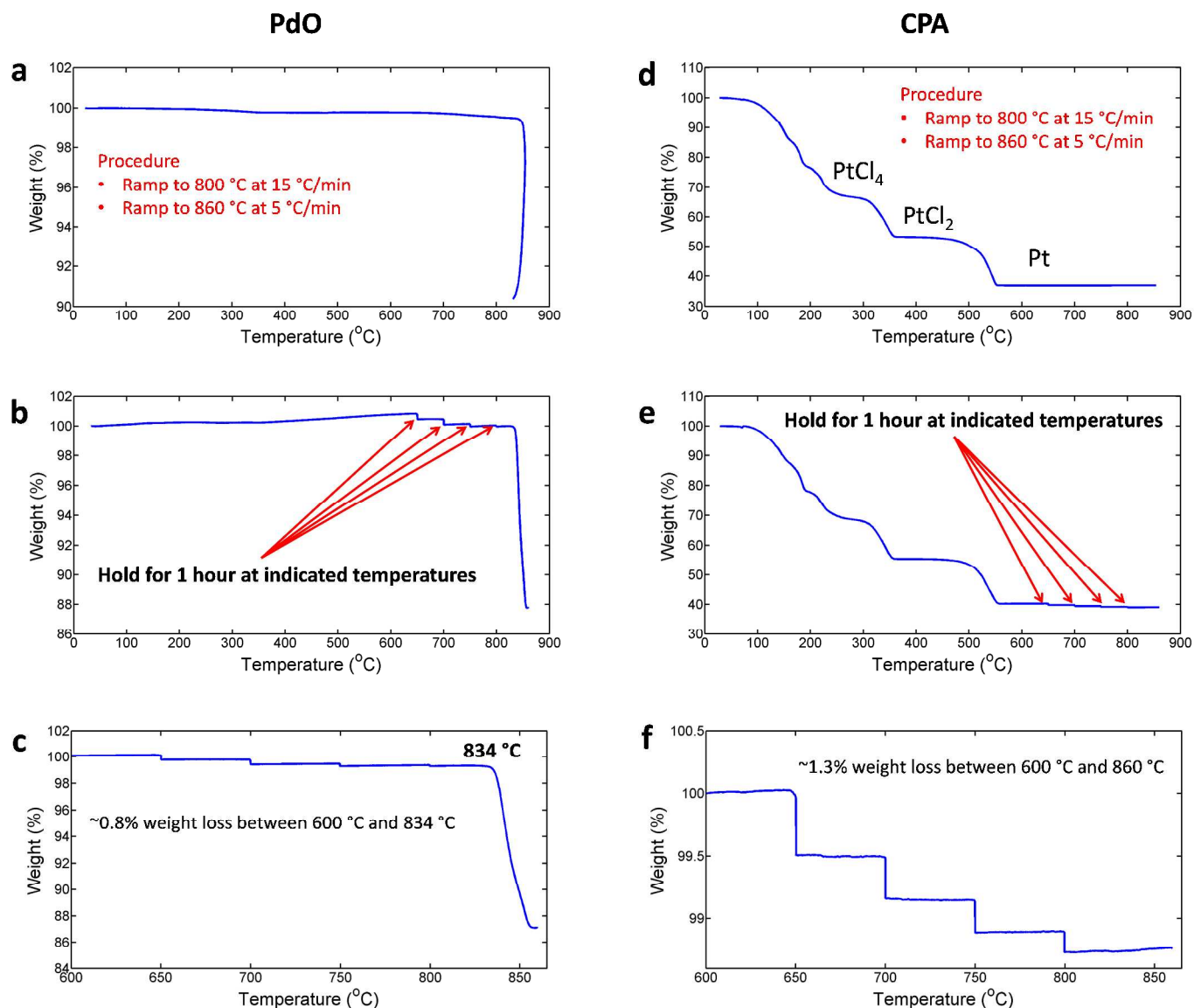


**Figure S4.** Percent of metal and oxide for sample 2 after various aging times at 650 °C in air, as determined by XPS. The results show that the transformation into metallic Pd is complete within 4 minutes.

### Thermogravimetric Analysis

Thermogravimetric analysis (TGA) shows that bulk PdO decomposes at ~830 °C to form Pd metal when heated in air (Figure S5a). We also performed a step wise heating of the sample to investigate the weight changes when the sample was held for 1 hr at the indicated temperatures (Figure S5b). A negligible additional weight loss (0.8 wt%) is seen when using the step wise heating procedure between 600 °C and 834 °C. This small weight loss during step wise heating may be caused by the limited stability of the TGA when doing isothermal temperature holds for 1 hour at each temperature. As we show later, with added Pt, a significantly greater degree of weight loss was seen over this same temperature range (Figure S5f). The decomposition curve for chloroplatinic acid (CPA) shows several plateaus consistent with the loss of water and then progressive loss of

Cl leading to the formation of metallic Pt around 550 °C indicating decomposition to metallic Pt, which is consistent with the TGA data reported in the literature<sup>3</sup> (Figure S5d). No further weight loss was seen over the temperature range of 600 °C – 860 °C when the sample was directly heated to this temperature. However, when the sample was heated in a stepwise fashion, we saw ~1.3% weight loss which we attribute to the residual chloride left on the sample (and confirmed by EDS analysis). Figure S5c and S5f show an expanded view of the weight changes happening on both the Pd and Pt samples when heated in a step wise fashion.



**Figure S5.** TGA curves of bulk samples in flowing air: (a) Aldrich PdO was ramped to 800 °C at 15 °C/min followed by ramping to 860 °C at 5 °C/min (b) PdO ramping to 650 °C at 15 °C/min and hold for one hour followed by incremental ramping by 50 °C and holding at the indicated temperatures for 1 hour until it reached 860 °C (c) Expanded view of the region between 600 °C – 850 °C from Fig. S5b showing a weight drop of 0.8% for temperatures between 600 °C and 834 °C before the onset of PdO decomposition (d) TGA plot for chloroplatinic acid (CPA); A similar temperature ramp was performed as in Figure S5a after the sample was calcined at 200 °C for 4 hours (e) TGA plot for CPA with the same heating ramp as in Figure S5b (f) Expanded



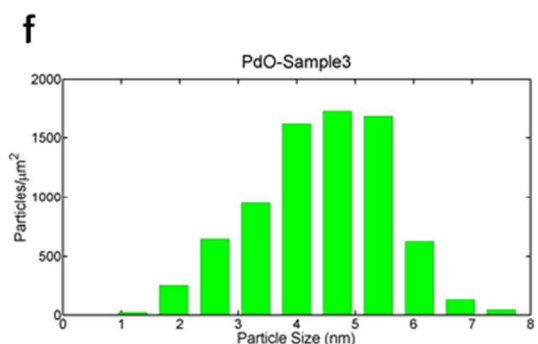
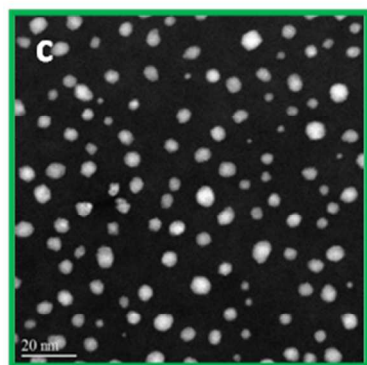
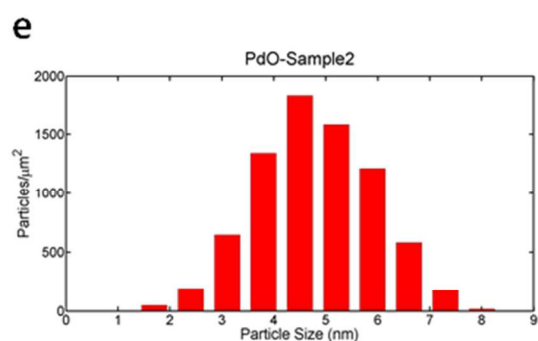
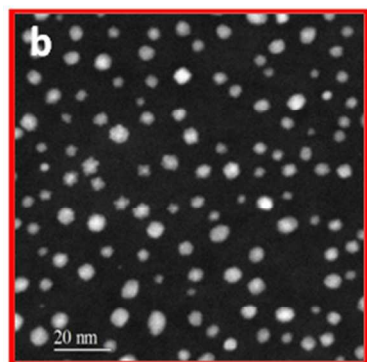
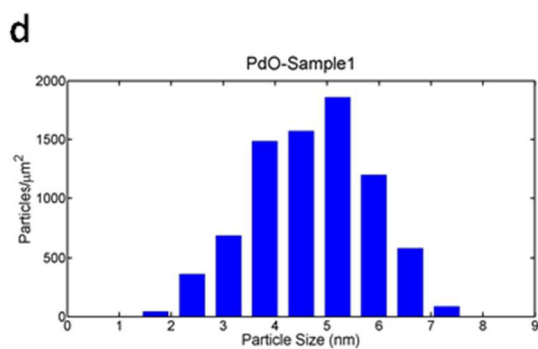
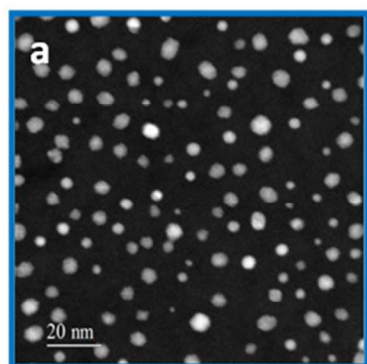
view of Figure S5e for temperatures above 600 °C, showing a weight drop of 1.3% for temperatures between 600 °C and 860 °C.

The weight change in the CPA+PdO sample between 600 °C to 860 °C (Fig. 4 in the manuscript) can now be compared with the corresponding weight changes for the PdO and the CPA by itself. We express the weight change as a % of the sample weight at 600 °C. The sample contained 50:50 Pt:Pd on an atomic basis. The bulk Aldrich PdO alone would lose 13 wt% upon decomposition, the Pt would lose 1.3 wt% and our mixed sample lost 7 wt%. Within the limits of experimental error, we see this weight change as being consistent with the transformation of the Pt+PdO sample into Pt-Pd over the temperature range 650 °C – 800 °C.

## **Particle Size Distributions for Replicate Samples**

Three samples were used to check for reproducibility at every step of the experiment (PdO, Pt+PdO, and Pt+PdO aged in air at 650 °C for two minutes). Figure S6 shows that all three PdO samples showed very similar sizes and morphologies along with similar number densities (particles/ $\mu\text{m}^2$ ).

After Pt deposition we saw a bimodal distribution of particles as seen by the HAADF-STEM images in Figure S7a-c. The samples consisted of smaller Pt particles surrounding the larger PdO particles, as determined by HRTEM and single particle EDS (Figure S2). The particle size distribution of the composite Pt+PdO sample suggested a logical cutoff in particle size based on the size distribution of the original PdO particle size distribution. We assumed a similar cut off for the aged samples (particles smaller than 2.7 nm are Pt while those larger contain Pd). We based this on the limited mobility of Pd hence we do not expect any Pd containing particle to have a size smaller than that seen in the original PdO sample. This is the basis for presenting the PSDs for these samples.

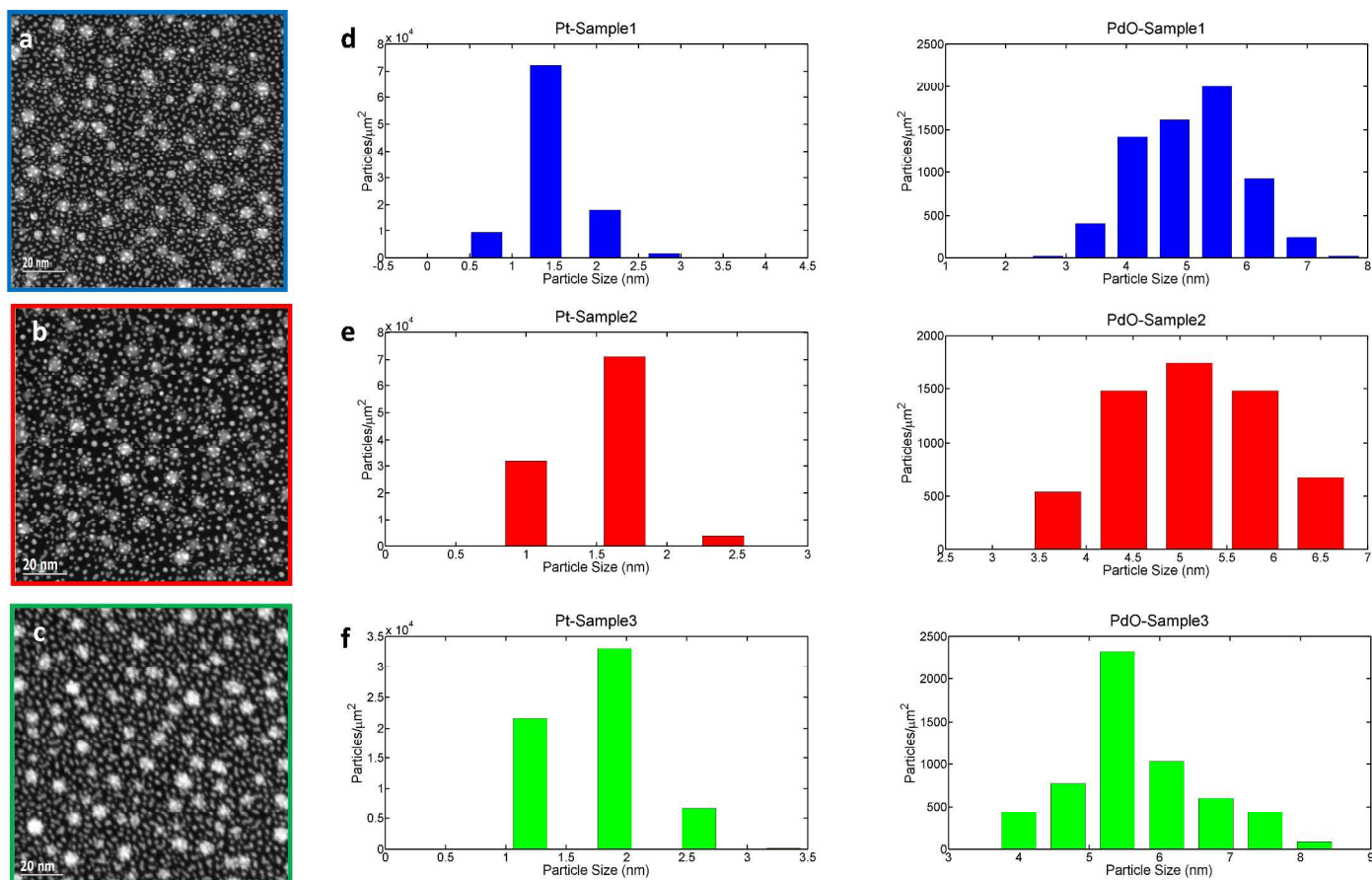


Sample	Average Size	Density
PdO	(nm)	(particles/μm²)
1	4.3 +/- 0.1	7885
2	4.4 +/- 0.1	7626
3	4.1 +/- 0.1	7691

**Figure S6.** HAADF-STEM of PdO nanoparticles formed after aging 5 Å of Pd/SiO<sub>2</sub> in air at 600 °C for two minutes: (a) Sample 1 (b) Sample 2 (c) Sample 3 (d-f) Corresponding particle size distributions for (a-c), respectively. The table below the figures summarizes the average size and number densities.

The second approach was to count the small Pt and large PdO particles separately. Both approaches gave similar statistical average particle sizes and number densities. Here we are reporting the separate size distribution for Pt and PdO as shown in Figure S7d-e.

## Pt+PdO



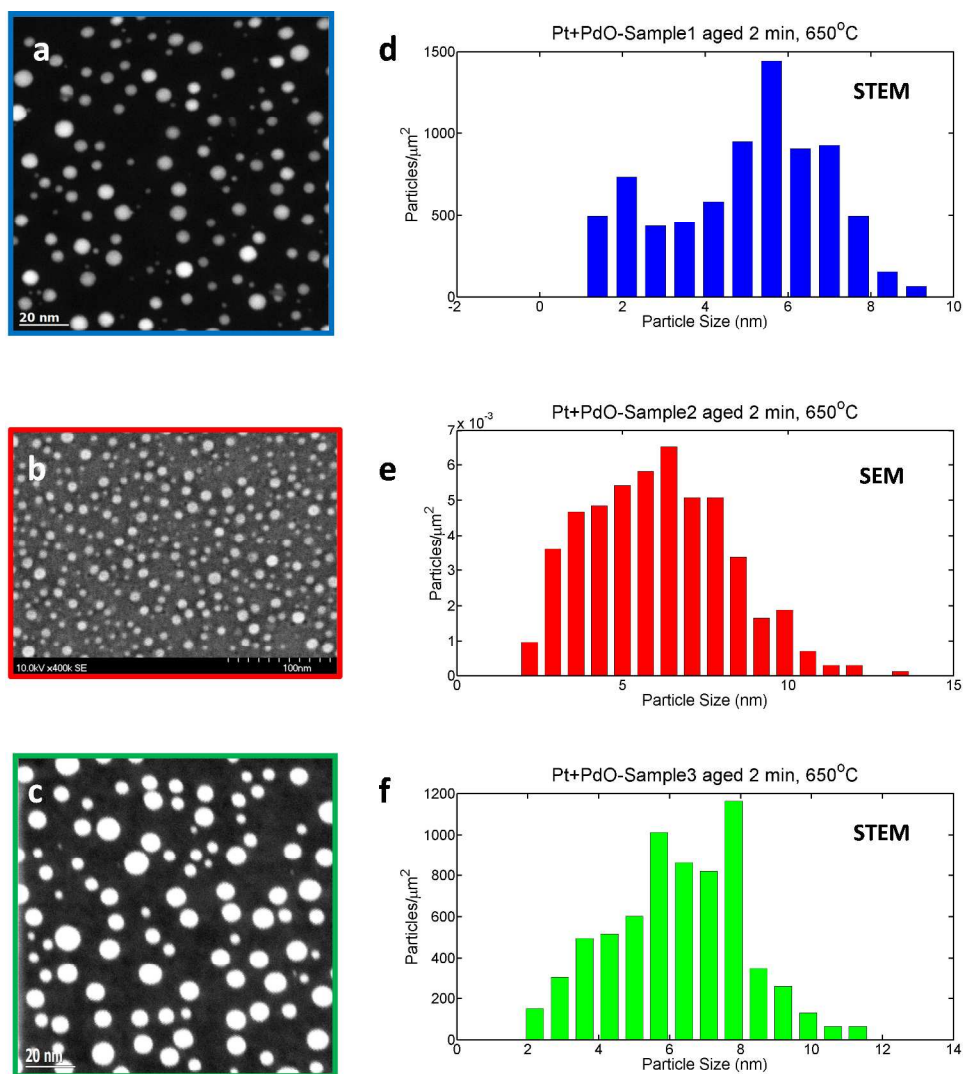
Sample	Pt Average Size	PdO Average Size	Pt density	PdO density
Pt+PdO	(nm)	(nm)	(particles/ $\mu\text{m}^2$ )	(particles/ $\mu\text{m}^2$ )
1	1.1 +/- 0.1	4.7 +/- 0.1	101296	6721
2	1.2 +/- 0.1	4.7 +/- 0.1	106634	5923
3	1.4 +/- 0.1	5.3 +/- 0.2	61695	5688

**Figure S7.** HAADF-STEM image after 5 Å Pt deposition (Pt+PdO) (a) Sample 1 (b) Sample 2 (c) Sample 3 (d-f) Corresponding separate Pt and PdO particle size distributions (PSDs) for (a-c), respectively. Summary of the statistics is presented below Figure S7.

Again, the Pt+PdO as prepared sample showed similar average particle sizes and number densities. Pt and PdO average sizes for sample 3 were slightly larger than the other two samples, thus, giving smaller number

densities. The Pt+PdO as prepared samples were aged in the reactor with flowing air (85 kPa) at 650 °C for two minutes. The HAADF-STEM images in Figure S8a-c reveal that the particles morphology has become more spherical and the average particle sizes increase. Figure S8d-f are the corresponding overall size distributions.

### Pt+PdO aged in air at 650 °C for two minutes



Sample	Pt Average Size (nm)	PdO Average Size (nm)	Pt density (particles/μm²)	Pt-Pd density (particles/μm²)
Pt+PdO aged 2 min, 650°C				
1	1.8 +/- 0.2	5.4 +/- 0.4	1551	6054
2 (SEM)	2.3 +/- 0.1	6.0 +/- 0.2	240	3603
3 (~665°C)	3.0 +/- 0.1	6.5 +/- 0.2	1884	5601

**Figure S8.** Pt+PdO aged in air at 650 °C for two minutes (a) HAADF-STEM image of Sample 1 (b) SEM image of Sample 2, hence, giving rise to larger average particle sizes. We could not get STEM images of sample 2 because the membrane window (electron transparent region) broke after aging. Therefore we obtained images from outside the membrane window in SEM (c) HAADF-STEM image of Sample 3. Sample 3 has

larger particles of both Pt and PdO compared to sample 1 and 2 possibly due to a slight overshoot to  $\sim 665^\circ\text{C}$  for a few 2-3 seconds during aging **(d-f)** Corresponding overall PSDs for (a-c), respectively. The cut-off size for samples 1 and 2 was 2.7 nm, whereas the cutoff size for sample 3 was 3.9 nm.

**Table S1. Summary of replicate sample statistics**

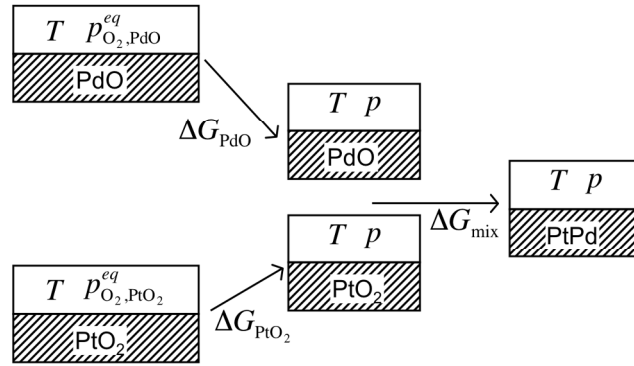
Summary of particle mean diameter and particle densities for three replicate samples that were prepared and aged to confirm the results reported here. Each sample started with PdO, then Pt was deposited to generate the Pt+PdO sample, after which it was aged in air at  $650^\circ\text{C}$  for two minutes.

Sample	Average Size	Density
PdO	(nm)	(particles/ $\mu\text{m}^2$ )
1	4.3 +/- 0.1	7885
2	4.4 +/- 0.1	7626
3	4.1 +/- 0.1	7691

Sample	Pt Average Size	PdO Average Size	Pt density	PdO density
Pt+PdO	(nm)	(nm)	(particles/ $\mu\text{m}^2$ )	(particles/ $\mu\text{m}^2$ )
1	1.1 +/- 0.1	4.7 +/- 0.1	101296	6721
2	1.2 +/- 0.1	4.7 +/- 0.1	106634	5923
3	1.4 +/- 0.1	5.3 +/- 0.2	61695	5688

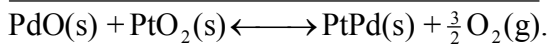
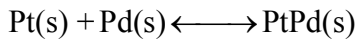
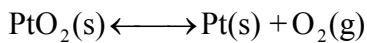
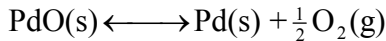
Sample	Pt Average Size	PdO Average Size	Pt density	Pt-Pd density
Pt+PdO aged 2 min, $650^\circ\text{C}$	(nm)	(nm)	(particles/ $\mu\text{m}^2$ )	( particles/ $\mu\text{m}^2$ )
1	1.8 +/- 0.2	5.4 +/- 0.4	1551	6054
2 (SEM)	2.3 +/- 0.1	6.0 +/- 0.2	240	3603
3 ( $\sim 665^\circ\text{C}$ )	3.0 +/- 0.1	6.5 +/- 0.2	1884	5601

# Thermodynamic analysis of the formation of metallic PtPd during heating of Pt and PdO in air

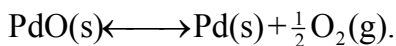


Scheme showing the thermodynamic steps in the *self-assembly* of metallic PtPd

We assume that Pt gives rise to a volatile  $\text{PtO}_2$  species under oxidizing conditions at high temperatures, some of which condenses on PdO islands or particles to initiate the self-assembly process. The overall reaction involves three steps: decomposition of PdO into  $\text{Pd} + \frac{1}{2} \text{O}_2$ , decomposition of  $\text{PtO}_2$  into  $\text{Pt} + \text{O}_2$  and alloying of Pt and Pd to form PtPd.



Consider the decomposition of PdO,



The equilibrium oxygen partial pressure  $p_{\text{O}_2}^{\text{eq}}$  for this reversible reaction has been reported to be<sup>4</sup>

$$\log(p_{\text{O}_2}^{\text{eq}}/p_{\text{O}_2}^0) = 15.8 - \frac{12300}{T},$$

where  $p_{\text{O}_2}^0 = 1 \text{ Pa}$  and  $T$  is in kelvins. At equilibrium the chemical potential of the reactants and products is equal. The equilibrium oxygen partial pressure at  $650^\circ \text{C}$  is  $298 \text{ Pa}$  using the equation listed above. We will next calculate the free energy change to bring the system to the oxygen pressure in the atmosphere. The local mean ambient pressure in Albuquerque is  $85 \text{ kPa}$ ,

implying a partial pressure of oxygen,  $p_{\text{O}_2} = 17.6 \text{ kPa}$ . The free energy change to bring  $\frac{1}{2}$  mole of  $\text{O}_2$  at PdO decomposition equilibrium pressure to the local pressure is given by

$$\Delta G_{\text{PdO}} = \frac{1}{2} RT \ln \left( \frac{p_{\text{O}_2}}{p_{\text{O}_2}^{\text{eq}}} \right).$$

Substituting the relation for equilibrium partial pressure of oxygen and rearranging one obtains

$$\Delta G_{\text{PdO}} = \frac{1}{2} RT \cdot \ln 10 \cdot \log \left( \frac{p_{\text{O}_2}}{p_{\text{O}_2}^0} \right) - 7.9 RT \cdot \ln 10 + 6150 R \cdot \ln 10.$$

One can use a similar approach for calculating the decomposition of  $\text{PtO}_2$ , which gives rise to 1 mole of  $\text{O}_2$ . The equilibrium oxygen partial pressure for this decomposition is<sup>4</sup>

$$\log(p_{\text{O}_2}^{\text{eq}}/p_{\text{O}_2}^0) = 15.8 - \frac{9200}{T}.$$

The corresponding change in free energy to bring the  $\text{PtO}_2$  to the ambient local pressure is given by

$$\Delta G_{\text{PtO}_2} = RT \cdot \ln 10 \cdot \log \left( \frac{p_{\text{O}_2}}{p_{\text{O}_2}^0} \right) - 15.8 RT \cdot \ln 10 + 9200 R \cdot \ln 10.$$

The formation of PtPd alloy is treated as an ideal mixture of equimolar Pt and Pd, all in the solid phase. The free energy of mixing is given by  $\Delta G = -RT \sum_i x_i \ln x_i$ , where  $x_i = 0.5$  for all the alloy components. Thus, the free energy of alloying per mole of PtPd is equal to  $\Delta G_{\text{mix}} = -0.693 RT$ .

Combining the free energies of the three thermodynamic steps one obtains the net free



energy for the decomposition of PtO<sub>2</sub> and PdO and alloy-formation of PtPd at any temperature and pressure as

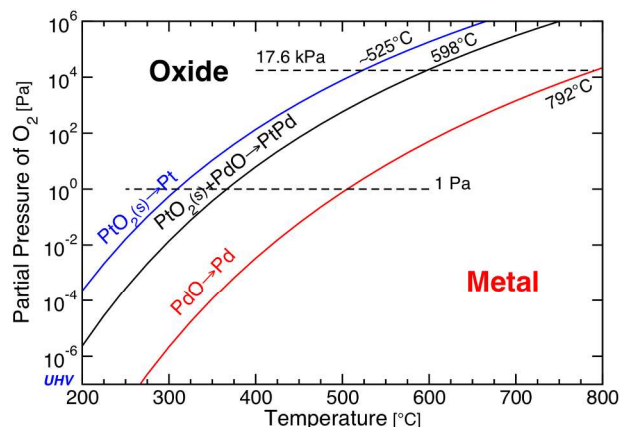
$$\Delta G = -RT \left( 55.26 - 3.45 \log \left( \frac{p_{O_2}}{p_{O_2}^0} \right) \right) + 35345 R.$$

per mol-PtPd. Employing this general relation one obtains a free energy of -17.8 kJ/mol-PtPd at 650 °C and 17.6 kPa, indicating the transformation of PdO to form Pt-Pd is thermodynamically feasible.

One can obtain the equilibrium curve ( $\Delta G = 0$ ) where PtO<sub>2</sub> causes transformation of PdO and to form the PtPd alloy using the equation listed above. This can be plotted as  $p_{O_2}(T)$  for this transformation. The equilibrium oxygen pressure for this transformation is given by

$$\log(p_{O_2}/p_{O_2}^0) = 16.0 - \frac{10233}{T}.$$

This relation is plotted in Figure S9 showing that PdO can be reduced to a metallic phase at lower temperatures in the presence of Pt.



**Figure S9.** Computed pressure of O<sub>2</sub> in equilibrium with PdO, PtO<sub>2</sub> and PtO<sub>2</sub>+PdO. The line is a phase boundary that divides the metal and oxide phases. The construction of this diagram is based on bulk thermodynamics.

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