

Supplementary Information: Mapping the thermal entrenchment behavior of Pd nanoparticles on planar SiO₂ supports

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1. Nanoparticle Synthesis

The various PEO-*b*-P2VP block copolymers used in the synthesis of Pd nanoparticles of different distributions are summarized in table S1. Figure S1 shows how the nanoparticle surface density and size changes with different synthesis conditions. It was observed that with oxygen plasma treatment before annealing, a distribution of small (< 5nm), high surface density features were achieved. On the other hand, without plasma, larger (5-20 nm), low surface density nanoparticles were obtained (S1 A). With different block copolymer chain lengths and Pd concentration in the solution, as shown in S1 B and C, a wide range of different sizes and surface densities were obtained. Figure S1 D shows that using the same concentration of Pd in the aqueous block copolymer solution, different densities can be obtained by changing the other two parameters.

Table S1 Different PEO-b-P2VP block copolymer chain lengths used for the synthesis of Pd nanoparticles.

Polymer	Mol. Weight of PEO block	Mol. Weight of P2VP Block
P0	1500	2800
P6	1800	1000
P7	7000	3500
P8	14000	2500
P9	21000	13500

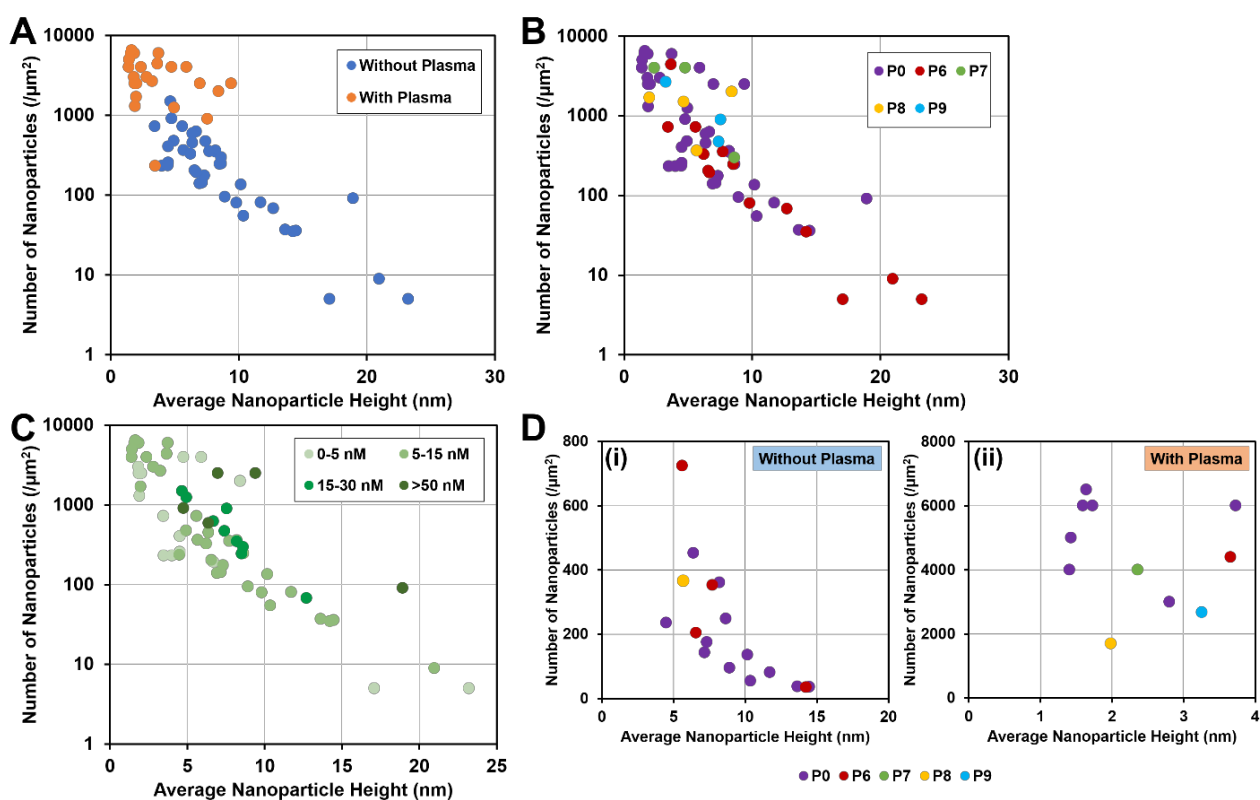


Figure S1 Range of different nanoparticle sizes and surface densities obtained by changing the synthesis conditions like using A) O_2 plasma treatment, B) different block copolymer chain lengths, C) different concentration of Pd precursor in the solution. D) Using a set concentration of Pd (12 nM) two very different distributions, (i) Large size, low surface density and (ii) Small size, high surface density, can be obtained using different polymers, without and with O_2 plasma treatment, respectively.

2. Outlying distributions

a. Small nanoparticles, low surface densities

Nanoparticles with smaller sizes and low surface densities (size ~ 1.3 nm, surface density ~ 100 nanoparticles/ μm^2), as shown in Figure S2, can be synthesized using very dilute Pd-block copolymer solutions. No clear nanopores or encapsulated nanoparticles are seen on the SiO₂ surface after heating (1040 °C for 10 min using a ramp rate of 3.3 °C/s) these nanoparticles since the particle size and density roughly matches the surface roughness of the bare SiO₂ surface. Thus, due to near-indistinguishable features from the SiO₂ wafer surface after thermal processing, these are excluded from consideration to avoid ambiguous inferences.

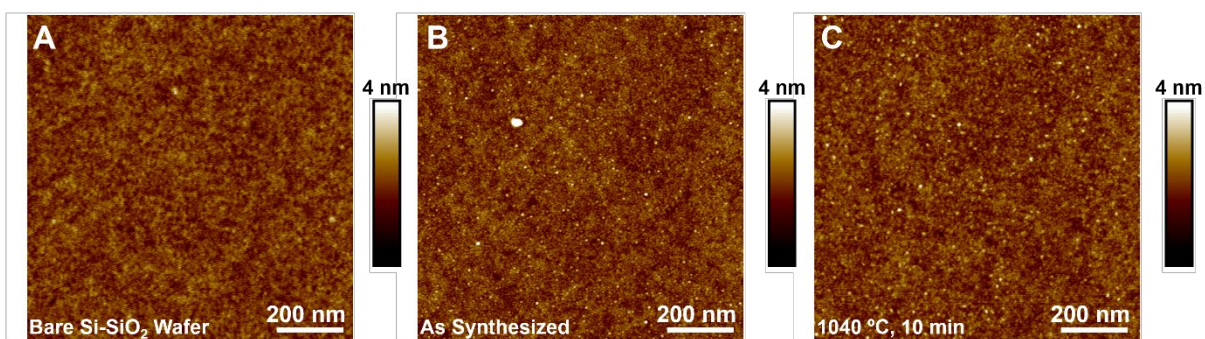


Figure S2 AFM images of A) bare Si-SiO₂ wafer surface, B) small, low surface density Pd nanoparticles as synthesized, and C) sample surface after heating at 1040 °C for 10 min using a ramp rate of 3.3 °C/s

b. Large nanoparticles, high surface densities

Pd nanoparticles with large sizes and high surface densities (size ~ 7 nm, surface density ~ 4000 nanoparticles/ μm^2) can be synthesized by using low spin coating rates, concentrated Pd solutions, and use of oxygen plasma. At these distributions, the nanoparticles on heating at 1040 °C for 10 min using a ramp rate of 3.3 °C/s show complete entrenchment (Figure S3). However, due to the high density of the nanopores

and low mobility of the large nanoparticles, minimal agglomeration is observed. Under these conditions, the nanopores overlap each other and make the SiO₂ surface extremely porous rendering the individual nanopore indistinct. These distributions are also excluded from consideration.

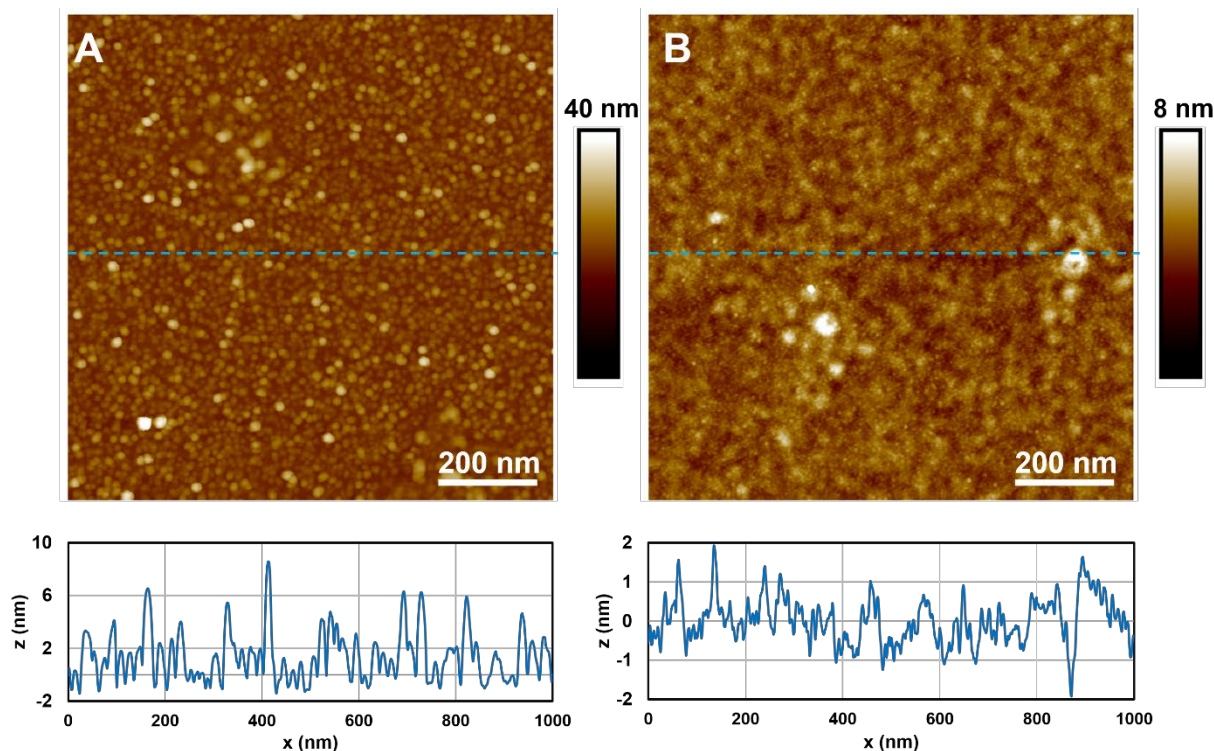


Figure S3 AFM images and line scans of A) large, high density Pd nanoparticles as synthesized and B) highly perforated SiO₂ surface after being heated at 1040 °C for 10 min using a ramp rate of 3.3 °C/s

3. Change in the volume of surface Pd with time

For small, high surface density nanoparticles, the particle mobility at temperatures above 800 °C is very high. Thus, these nanoparticles tend to agglomerate with time. There are also mechanisms like evaporation of the surface Pd atoms and diffusion of Pd into the SiO₂ surface that are enhanced at high temperatures. In order to quantify the role of agglomeration and diffusion and evaporation in the changing nanoparticle distribution with time, the apparent volume of the Pd on the surface was calculated and is shown in Figure

S4 and Table S2. Any material loss would be attributed to either diffusion or evaporation since these two cannot be distinguished between. However, within error, no material loss was observed and the amount of Pd present before and after heating can be reconciled. Thus, the change in nanoparticle size and surface density can be attributed to agglomeration and other surface effects are considered to be negligible.

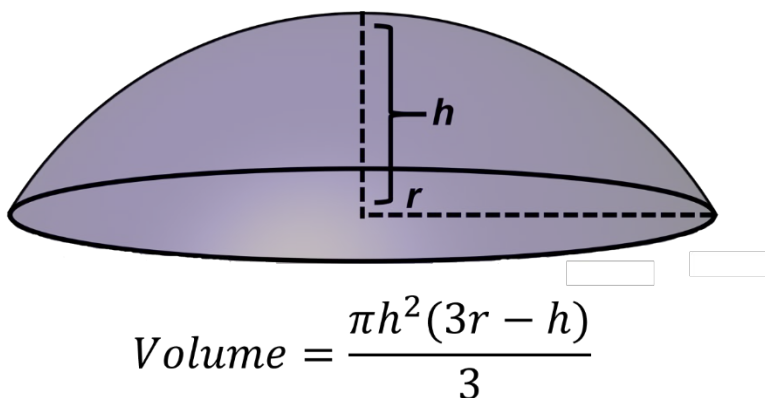


Figure S4 For calculating the total volume of the surface Pd with changing sizes and densities the shape of each Pd nanoparticle is assumed to be that of a truncated sphere.

Table S2 Summary of nanoparticle height, radius, surface density, and total calculated volume as a function of time at 1040 °C (reached using a ramp rate of 3.3 °C/s)

Time at 1040°C (min)	Nanoparticle Height h (nm)	Nanoparticle Radius r (nm)	Number of Nanoparticles ($/\mu\text{m}^2$)	Volume of Surface Pd ($\text{nm}^3/\mu\text{m}^2$)
0	1.56 ± 0.62	1.51 ± 0.63	6000	45×10^3
1.5	3.74 ± 1.84	11.21 ± 3.34	140	61×10^3
3	4.82 1.75	9.81 ± 3.03	70	42×10^3

4. Range of behaviors observed

Different behaviors (complete and partial entrenchment, agglomeration, and encapsulation) are observed across different sizes and surface densities of Pd

nanoparticles. Particularly, we observe that nanopore formation, either with partial or complete entrenchment, occurs almost across the range of nanoparticle sizes and surface densities with different degrees of aggregation (Figure S5).

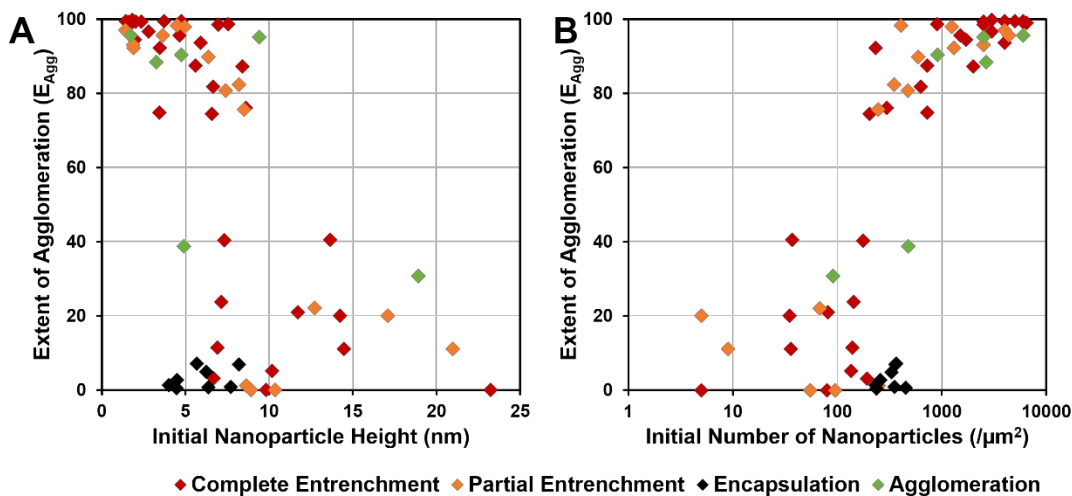


Figure S5 Different behaviors (Complete and partial entrenchment, encapsulation, and agglomeration) and degrees of aggregation preceding nanopore formation (E_{Agg}) observed as a function of A) initial nanoparticle size and b) initial nanoparticle surface density for Pd nanoparticles heated to 1040 °C for 10 minutes at 3.3 °C/s.

5. Extended heating of partially entrenched and agglomerated nanoparticles

In identifying the various behaviors of nanoparticles of different sizes and surface densities on heating at 1040 °C for 10 minutes at 3.3 °C/s, specific ranges of extent of agglomeration (E_{Agg}) and pore fraction (f_{Pore}) are defined. Nanoparticles that exhibit partial entrenchment ($10\% < f_{Pore} < 75\%$) and agglomeration without entrenchment ($E_{Agg} > 10\%$ and $f_{Pore} = 0\%$) are subjected to extended heating. We observe that in both cases, the additional heating step leads to further nanopore formation (Figure S6). For the partially entrenched nanoparticles, the f_{Pore} increases from 50% to 90 % on extended heating (Figure S6 A). For the agglomerated nanoparticles, several nanopores are observed and

the f_{Pore} increases from 0% to 45% on extended heating. These trends show that most nanoparticle distributions, except those that get encapsulated, will undergo complete entrenchment, albeit at different rates. The rate of entrenchment of larger nanoparticles or high density nanoparticles that form large aggregates, will be slower than the smaller nanoparticles.

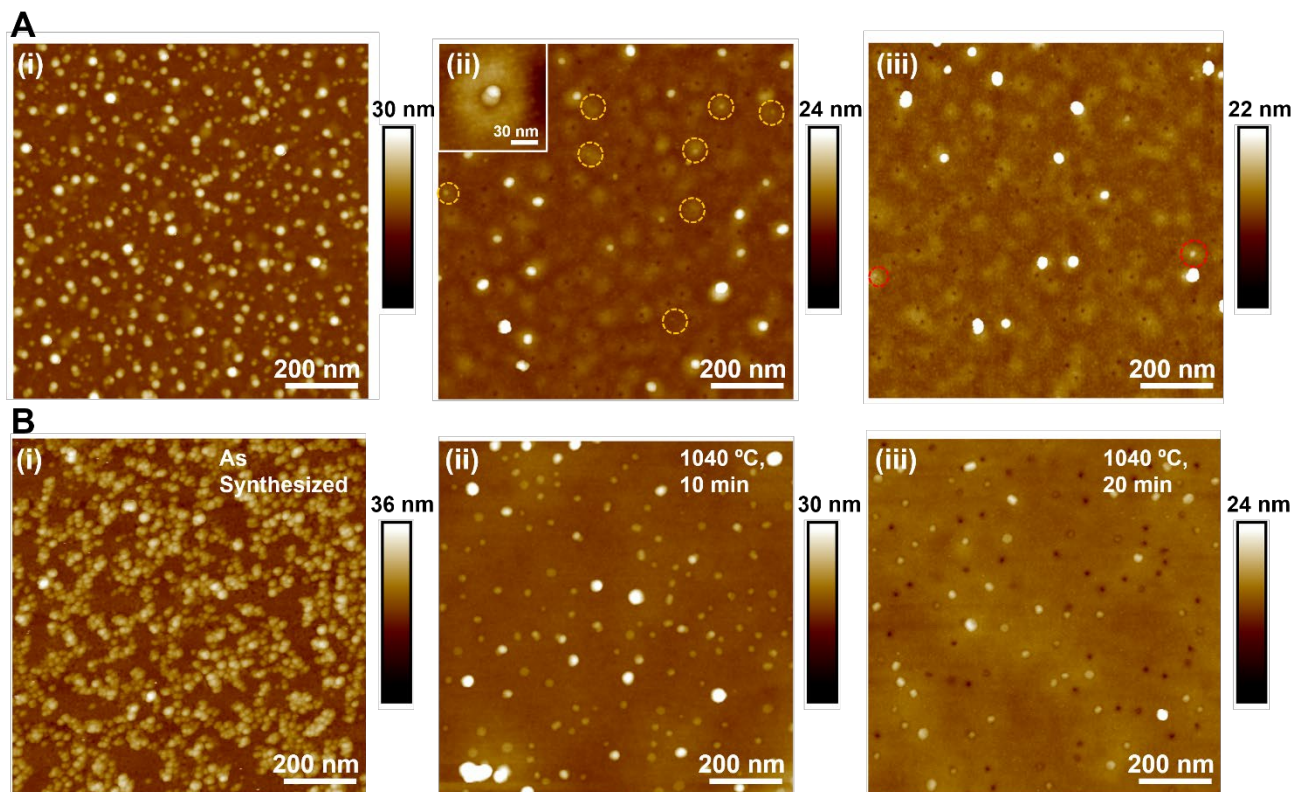


Figure S6 A) AFM images of Pd nanoparticles i) as synthesized (size ~ 7 nm, surface density ~ 500 nanoparticles/ μm^2), that show ii) partial entrenchment ($f_{pore} = 50\%$) after heating for 10 minutes at 1040 °C with several *nearly-entrenched* nanoparticles (dotted circles, inset) which iii) entrench almost entirely ($f_{pore} = 90\%$) after extended heating for 20 minutes at 1040 °C with very few *nearly-entrenched* nanoparticles (dotted circles) B) AFM images of Pd nanoparticles i) as synthesized (size ~ 10 nm, surface density ~ 2500 nanoparticles/ μm^2), that exhibit ii) agglomeration without nanopore formation ($f_{pore} = 0\%$) on heating for 10 minutes at 1040 °C, which iii) on extended heating for 20 minutes at 1040 °C leads to nanopore formation ($f_{pore} = 45\%$) in the SiO₂ surface.

6. Etching partially embedded Pd nanoparticles

Larger Pd nanoparticles that are spaced far apart, have very low surface mobility and show no agglomeration. These nanoparticles, on heating at 1040 °C for 10 minutes, do not exhibit nanopore formation but show a reduction in the nanoparticle height due to partial embedding in the SiO₂ surface. On etching the Pd from the surface, the oxide ridges and the trenches left behind by the nanoparticles can be clearly seen thus, demonstrating that the Pd nanoparticles are not encapsulated in SiO₂. (Figure S7).

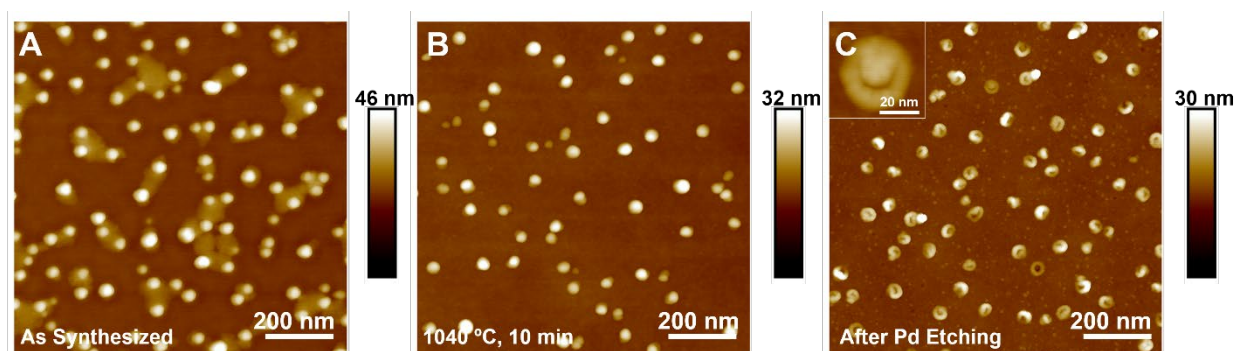


Figure S7 AFM images of A) Pd nanoparticles that show no nanopore formation but only B) partial embedding in the SiO₂ surface on heating at 1040°C for 10 minutes, can be C) etched away to reveal the oxide ridges and the trenches formed by the partial entrenchment

7. Surface distribution trends for encapsulated nanoparticles

Nanoparticle distributions that lead to encapsulation of nanoparticles have the same surface density of encapsulated features as the initial nanoparticles (Figure S8 A) showing that these particles are laterally immobile and do not agglomerate. However, the final size of the encapsulated features may be less or similar to the initial nanoparticle size (Figure S8 B). This shows that the nanoparticles may be partially embedding in the surface before encapsulation in some cases or that the height of the ridges formed around the nanoparticles is comparable to that of the initial nanoparticle.

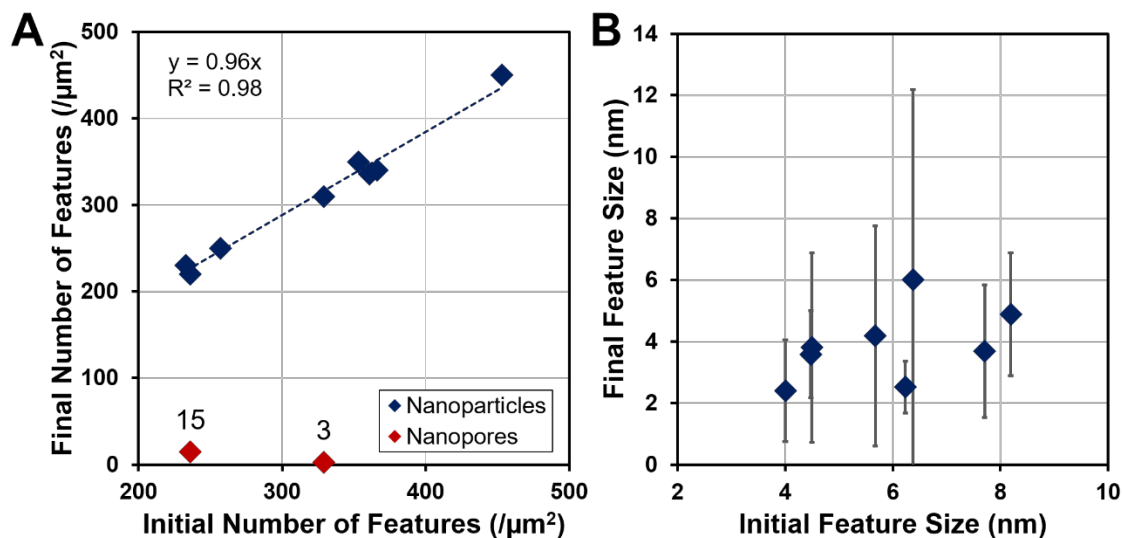


Figure S8 A) Feature density and B) feature size of encapsulated nanoparticles before and after rapid thermal processing at 1040 °C for 10 min using a ramp rate of 3.3 °C/s

8. Initial distributions for studying the different heating conditions

The nature of nanopore formation at different heating conditions (temperature, hold time, ramp rate) is studied for two different surface distributions of Pd nanoparticles. These distributions are illustrated in Figure S9. For the smaller, high surface density nanoparticles (Figure S9 A), there is high tendency of the nanoparticles to agglomerate so the effect of both agglomeration and nanopore formation can be studied simultaneously. The larger, low surface density nanoparticles (Figure S9 B) have a low surface mobility and thus do not agglomerate aggressively. For this distribution, nanopore formation without the influence of agglomeration is studied.

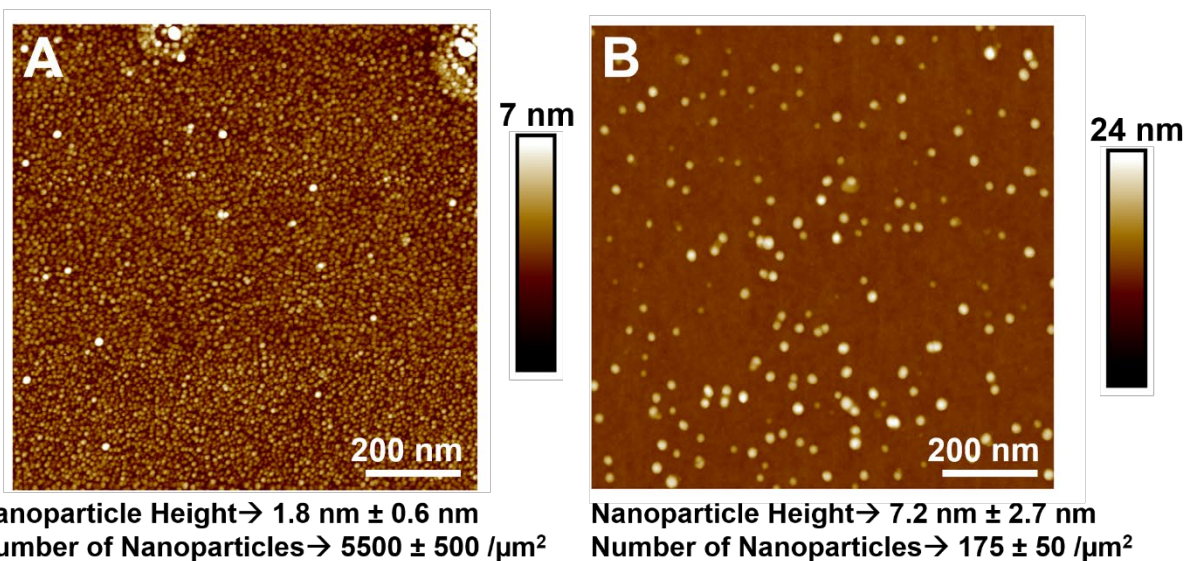


Figure S9 AFM images of initial distributions of Pd nanoparticles on SiO₂ surface used to study the different heating conditions. A) High surface density, small sized nanoparticles that tend to agglomerate, B) low surface density, large nanoparticles that have low surface mobility.

9. Increasing ramp rates above minimum values

We observe that a minimum ramp rate of 3.3 °C /s is needed to observe clear nanopore formation. However, increasing the ramp rate of heating does not affect the nature of nanopore formation so long as it is above the minimum values (Figure S10).

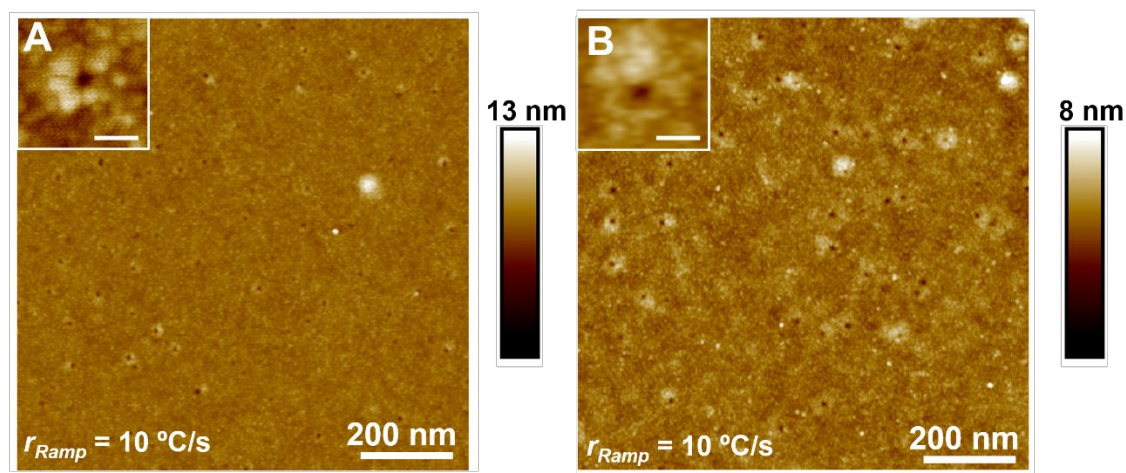


Figure S10 AFM images of A) small, high surface density and B) large, low surface density Pd nanoparticles on SiO₂ heated using ramp rates (r_{Ramp}) 10 °C/s to 1040 °C and held for 10 min.

10. Designing Nanopores of Desired Dimensions

The nanopores formed by thermal processing of metal nanoparticles on SiO₂ supports can be tuned to achieve a range of nanopore diameters. The different synthesis conditions (concentration of Pd in block co-polymer micelle solution, chain lengths of block copolymers used, oxygen plasma) that lead to increasing nanopore diameters are summarized in Table S3. We observe that nanopores of the same diameter can be achieved using two distributions of nanoparticles, with or without agglomerations (Figure S11). However, without agglomeration, tall oxide ridges will accompany the nanopores. If oxide ridges are not desired, nanopores of comparable diameters can be achieved via agglomeration. The nanopore diameter may thus be tuned between 5-25 nm by varying the synthesis condition.

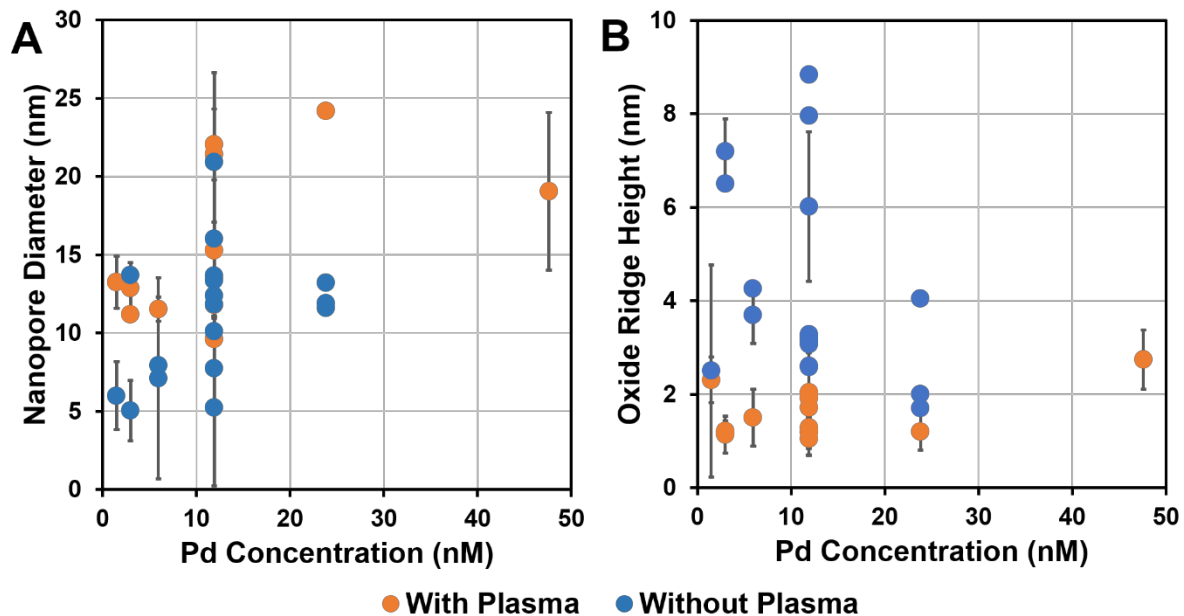


Figure S11 A) Diameters of nanopores and B) heights of oxide ridges formed after heating to 1040 °C for 10 minutes at 3.3 °C/s as a function of synthesis conditions (concentration of Pd in the block copolymer micelle solution and use of oxygen plasma) of the Pd nanoparticles.

Table S3 Summary of synthesis conditions used in the block copolymer micelle mediated synthesis of Pd nanoparticles of different distributions.

Table gives nanopore distributions and extents of agglomeration heating to 1040 °C for 10 minutes at 3.3 °C/s.

Pd Concentration (nM)	Block Co-polymer	O₂ Plasma	Initial NP Height (nm)	Initial Number of NP (μm⁻²)	Nanopore Diameter (nm)	Oxide Ridge Height (nm)	Number of Nanopores (μm⁻²)	E_{Agg} (%)
3.0	P6	No Plasma	6.7 ± 1.6	193	5.0 ± 1.2	7.2 ± 2.9	176	<20
11.9	P0	No Plasma	7.2 ± 2.6	143	5.3 ± 1.3	6.0 ± 2.7	97	20-40
1.5	P6	No Plasma	3.4 ± 1.4	725	6.0 ± 0.5	2.5 ± 1.2	180	60-80
6.0	P0	No Plasma	6.9 ± 2.5	140	7.1 ± 1.3	3.7 ± 1.7	120	<20
11.9	P0	No Plasma	7.3 ± 2.1	176	7.7 ± 1.8	3.2 ± 1.9	95	40-60
6.0	P6	No Plasma	9.8 ± 2.0	80	7.9 ± 4.7	4.3 ± 2.5	70	<20
11.9	P8	5min, 15 Watt	2.0 ± 1.0	1700	9.6 ± 1.5	2.0 ± 0.7	84	80-100
11.9	P0	No Plasma	13.6 ± 5.9	37	10.1 ± 2.2	8.0 ± 2.2	20	20-40
3.0	P0	5min, 60 Watt	2.0 ± 1.2	2500	11.2 ± 0.2	1.1 ± 0.4	15	80-100
6.0	P0	5min, 60 Watt	1.9 ± 1.0	6000	11.5 ± 0.8	1.5 ± 0.6	40	80-100
23.8	P8	No Plasma	4.7 ± 2.4	1500	11.6 ± 0.4	1.7 ± 0.9	50	80-100
11.9	P0	5min, 30 Watt	2.8 ± 0.6	3000	11.8 ± 0.7	1.2 ± 0.3	100	80-100
11.9	P6	No Plasma	5.6 ± 1.5	725	11.8 ± 0.7	2.6 ± 1.7	90	80-100

23.8	P0	No Plasma	6.7 ± 1.8	627	11.9 ± 0.8	4.1 ± 1.2	100	80-100
11.9	P0	No Plasma	10.2 ± 2.0	136	12.4 ± 1.0	3.2 ± 0.8	117	<20
3.0	P0	5min, 60 Watt	1.8 ± 0.8	3000	12.9 ± 1.6	1.2 ± 0.2	5	80-100
23.8	P7	No Plasma	8.6 ± 3.4	297	13.2 ± 1.9	2.0 ± 0.5	60	60-80
1.5	P7	5min, 30 Watt	4.8 ± 2.0	4000	13.3 ± 1.7	2.3 ± 0.5	20	80-100
11.9	P6	No Plasma	6.6 ± 4.2	204	13.4 ± 1.6	3.3 ± 1.3	50	60-80
11.9	P7	5min, 60 Watt	2.4 ± 0.9	4000	13.5 ± 2.6	2.0 ± 0.6	26	80-100
11.9	P0	5min, 30 Watt	1.6 ± 0.6	6500	13.6 ± 1.8	1.7 ± 0.7	60	80-100
11.9	P0	No Plasma	11.7 ± 4.6	81	13.7 ± 1.9	3.1 ± 0.7	60	<20
3.0	P6	No Plasma	23.2 ± 2.8	5	13.7 ± 5.0	6.5 ± 1.6	5	<20
11.9	P0	5min, 60 Watt	1.6 ± 0.7	6000	15.3 ± 1.8	1.0 ± 0.3	41	80-100
11.9	P6	No Plasma	14.2 ± 2.5	35	16.0 ± 2.2	8.8 ± 2.3	27	<20
47.6	P0	5min, 60 Watt	7.0 ± 3.1	2500	19.1 ± 5.0	2.7 ± 0.6	35	80-100
11.9	P0	No Plasma	14.5 ± 4.1	36	20.9 ± 6.4	2.6 ± 0.6	30	<20
11.9	P0	5min, 45 Watt	1.4 ± 0.9	5000	21.4 ± 5.2	1.3 ± 0.6	27	80-100
11.9	P0	5min, 60 Watt	3.7 ± 0.8	6000	22.1 ± 2.3	1.9 ± 1.0	31	80-100
23.8	P9	5min, 30 Watt	7.5 ± 2.6	900	24.2 ± 0.3	1.2 ± 0.4	9	80-100