Supporting Information.

Experimental Section:

Materials

Platinum(II)-acetylacetonate (Pt(acac)$_2$) (98% purity) was purchased from STREM Chemicals and used as received. Styrene was purchased from Sigma Aldrich and distilled prior utilization to remove the inhibitor. Sodium para-styrene sulfonate, ammonium peroxodisulfate (APS) and sodium dodecyl sulfate (SDS) were purchased from Sigma Aldrich and used as received. Platinum standards (AAS or ICP grade) were received from Chemlab (Zedelgem, Belgium) and diluted with water (milliQ grade) to obtain standard solutions for the ICP-OES measurements. Ultrapure water (milliQ grade) was used throughout the experiments.

Synthesis

Platinum-complex containing polymer particles

Platinum acetylacetonate containing latex particles were produced by surfactant free emulsion polymerization. The exact amounts described here were used for the synthesis of the smallest particles prepared for the seeding process; the amounts used for the synthesis of particles with different amounts of platinum acetylacetonate are put in brackets. 115 mL of water was heated to 80 °C and degassed for 30 min with argon to remove oxygen. 4000 (7500) mg of styrene, containing 160 mg (various amounts) of platinum(II) acetylacetonate, was added and stirred mechanically (1000 rpm). Consecutively, 35 (15) mg sodium para-styrene sulfonate dissolved in 5 ml water and 75 (50) mg of ammonium peroxodisulfate (APS) dissolved in 5 ml water were added. The mixture was allowed to react for 24 hours under argon atmosphere. Subsequently, the dispersion was dialyzed extensively against water using dialysis membranes with a molecular weight cutoff of 14000 g/mol (Visking membranes, Carl Roth, Germany). The dialysis process was stopped once the water phase showed conductivity lower than 2 mS/m.

Inductively coupled plasma – optical emission spectrometry (ICP-OES)

All measurements were performed with an ACTIVA M spectrometer (Horiba Jobin Yvon, Bernsheim, Germany) equipped with a Meinhardt-type nebulizer, a cyclone chamber and controlled by ACTIVAnalyst 5.4 software.

The following instrumental conditions were applied: 1250 W forward plasma power, 12 L·min^{-1} Ar flow and 15 rpm pump flow. The colloidal dispersions measured were diluted with ultra pure water to 0.1 wt-% of colloids and sonicated for 3 minutes prior to measuring. Sodium dodecyl sulfate (SDS) was added to both metal standards and colloidal dispersions to a concentration of 0.75 wt.-%; following a measurement protocol established recently.[19]

The argon emission line at 404.442 nm was used as reference line. Measurements were performed using 4 different standard concentrations and 5 s integration time. As baseline correction, a dynamic underground correction provided by the software was used. The emission lines chosen for the platinum determination were 204.951 nm, 212.863 nm, and 270.240 nm.

Substrate and deposition of colloids

Silicon wafers from CrysTec (Berlin, Germany) (orientation: (100), dopant: phosphor, specific resistance: < 0.2 Ohm•cm, front side: polished, backside: etched) were used as substrates.

Pieces of 5 × 10 mm were cleaned with organic solvents (3 min in acetone Selectipur plus 3 min in 2-propanol Selectipur from BASF) in an ultrasonic bath (Merck eurolab) at 50 °C. The substrates were exposed to oxygen plasma leading to a strongly hydrophilic surface. After diluting the dispersions to 0.5 wt.-% solid content with purified water, a drop with a volume of 0.5 µl was deposited on the polished side of the substrate. Evaporation of the water took place at ambient conditions.

Plasma treatment

The oxygen plasma was delivered by a commercial etching machine (Oxford Plasmalab 80 Plus RIE) including an ICP (inductively coupled plasma) source. The following plasma parameters were applied for the pre-treatment of the substrate before depositing the solution on it, as well as for the reduction of the diameter of the particles: O_2: 20 sccm; ICP power: 100 W; DC-bias: -12 V; total pressure: 80 mTorr; nominal substrate temperature: 20 °C. Before using the isotropic plasma described above, oxygen plasma with a more anisotropic component was used to chop the contact areas between the polymer particles and separate them. This guarantees the conservation of the original hexagonal order during the ashing procedure. The plasma parameters in this case were: O_2: 50 sccm; ICP power: 200 W; DC bias: -89 V; total pressure: 80 mTorr; nominal substrate temperature: 20 °C. To completely separate the particles, the anisotropic plasma was applied for 20-50 s.

In the RIE-process to etch the silicon substrate, a mixture of CHF3/CF4 (20:2 sccm) was utilized with a radiofrequency (RF) power of 40 W and a DC-bias of -97 V.

Annealing

All samples were annealed in a commercially available lamp furnace (UniTemp RTP-1200-100) under the following conditions: oxygen atmosphere; pressure: 2 mbar (1 mbar = 100 Pa); heating rate: 0.6 °C/s; maximal temperature: 1100 °C; time at maximal temperature: 10 min.

Analysis

The samples were analyzed using the Hitachi S5200 HRSEM with an acceleration voltage of 30 kV guaranteeing a resolution of 0.5 nm. The images (Pt NP size and distances) were analyzed further by the program ImageJ.

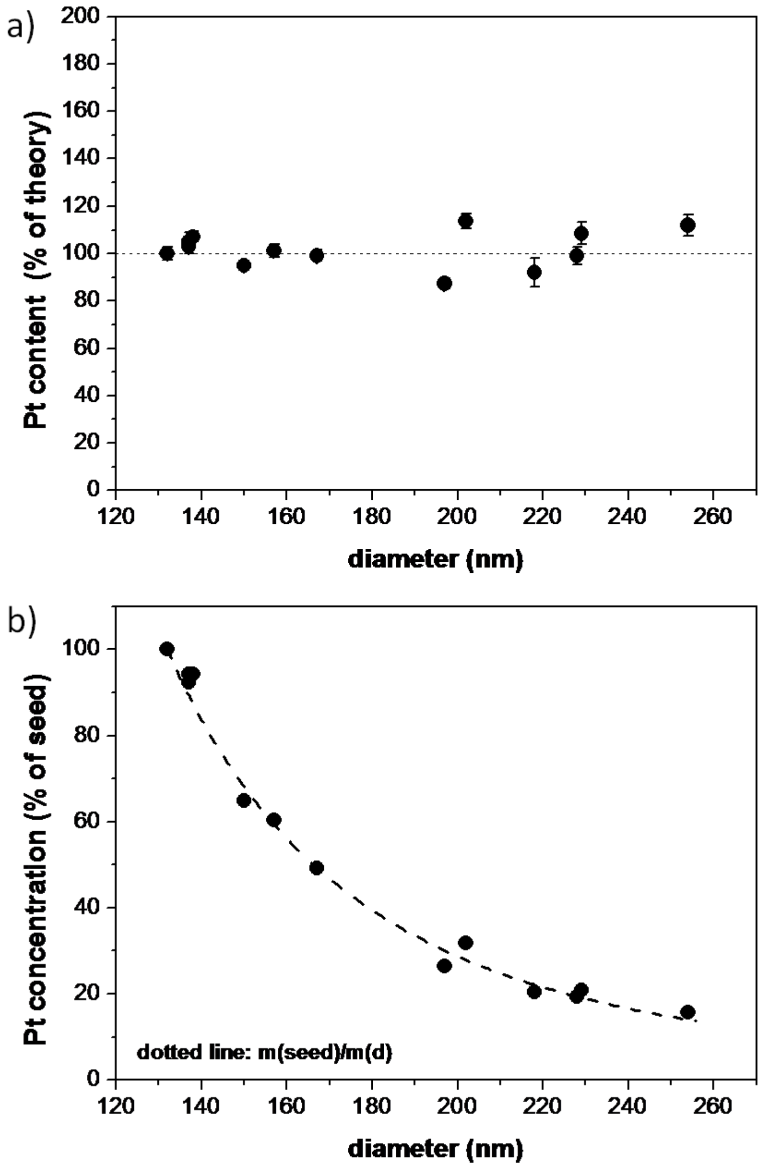

Figure S1. (Supplementary to Figure 1) Platinum concentration inside the polymer particles synthesized by a seeded polymerization from the same seed particles measured by ICP-OES. a) Measured platinum content for the different sizes obtained by the process plotted in percent of the expected, theoretical value. The measured values are all close to the theoretical content, indicating that no loss of platinum occurs during the reaction. b) Measured platinum amount given in percent of the seed particles. As the size of the particles increases and no further platinum is added, the platinum concentration decreases linear with the increase in mass. The dotted line shows the relation between mass of a seed particle and mass of the final particle produced by the seeding process. The measured platinum values follow that relation closely.

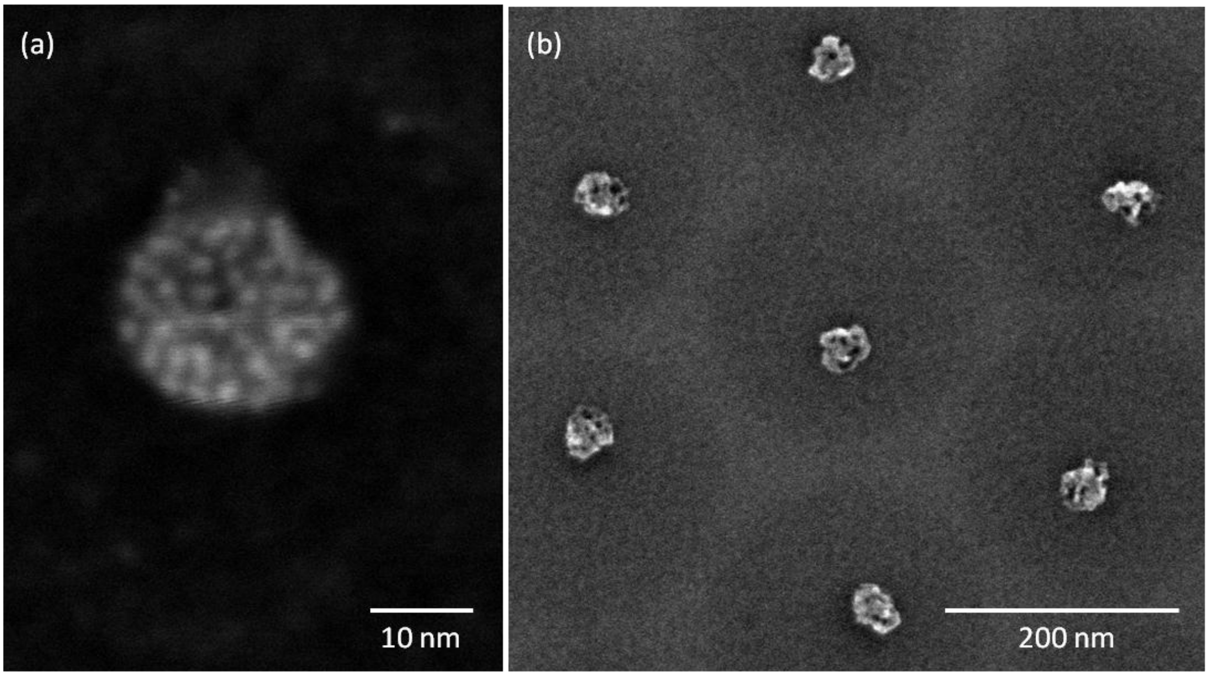

Figure S2. SEM images of Pt complex containing PS particles, after oxygen plasma treatment to decrease their size. The initial diameter of the latexes was 175 nm (a) and 254 nm (b). After an exposure of 60 min to isotropic oxygen plasma the diameter of the residual heterogeneous particles is decreased to 27 nm (a) and 39 nm (b), respectively.

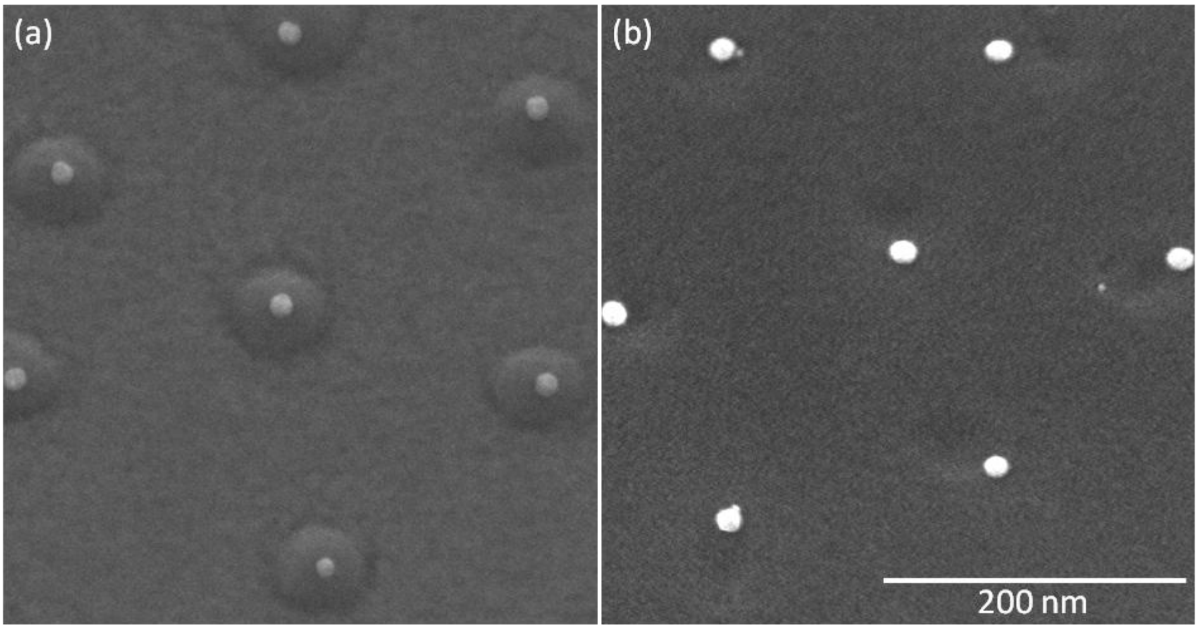

Figure S3. a) Pt NPs on top of a silicone oxide elevation. Due to the catalytic effect of Pt the oxide growth under and around the particles is enhanced during annealing. b) Effect of hydrofluoric acid treatment after the annealing procedure. The silicon oxide was removed and the Pt NPs still exhibit their hexagonal order. As the oxide also grows faster under the Pt NPs during annealing, small depressions are visible on the SEM image (sample tilted by 30°).

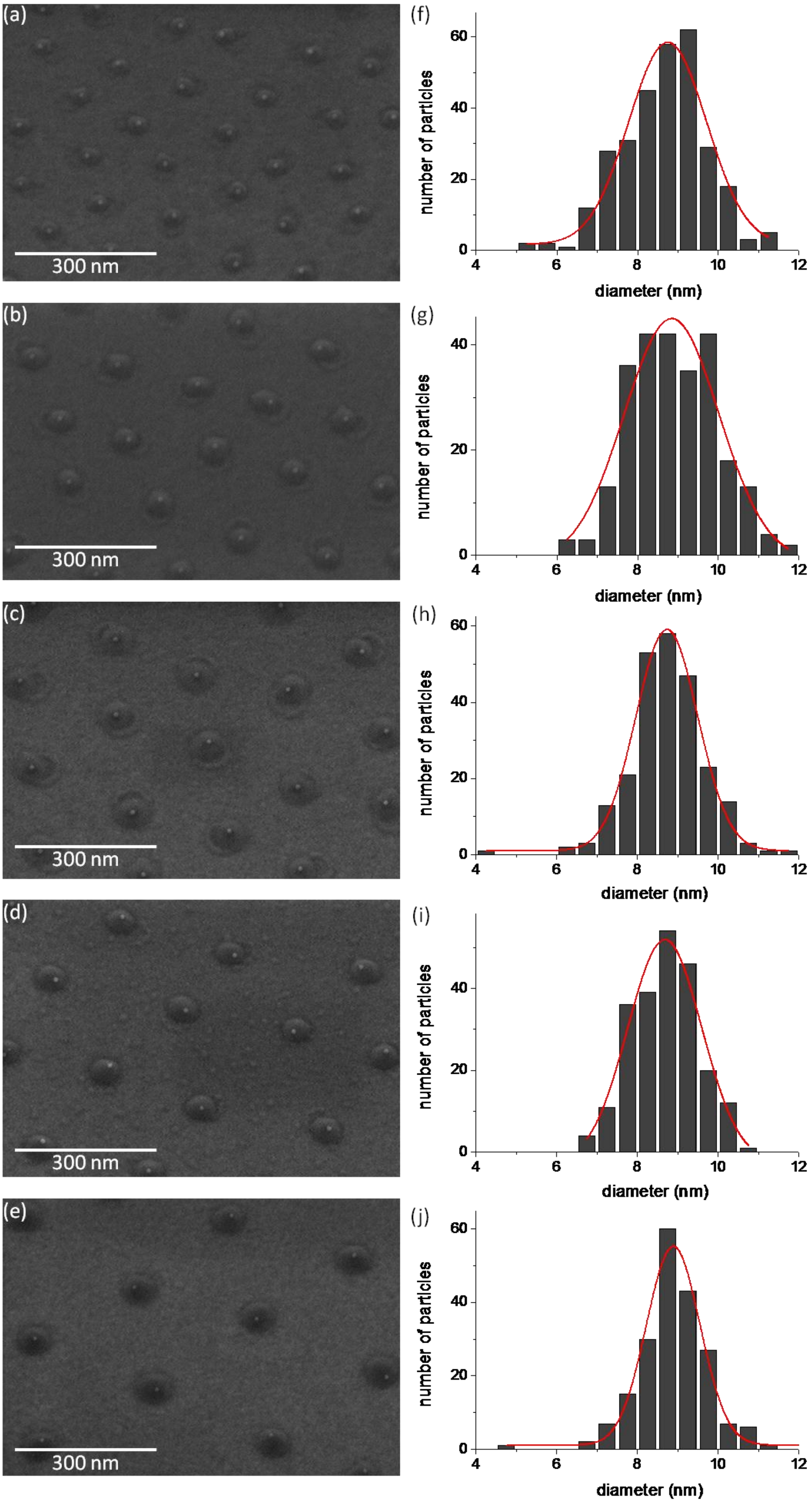
(a)
300 nm
(f)
number of particles
0
20
40
60
4
6
8
10
12
diameter (nm)
(b)
300 nm
(g)
number of particles
0
20
40
diameter (nm)
(c)
300 nm
(h)
number of particles
0
20
40
60
diameter (nm)
(d)
300 nm
(i)
number of particles
0
20
40
diameter (nm)
(e)
300 nm
(j)
number of particles
0
20
40
60
diameter (nm)

Figure S4. The SEM images (a-e) demonstrate that the average Pt particles distance can be varied from 130 nm (a) to 250 nm (e) while keeping the particle diameter constant at 9 nm as shown in the corresponding diameter histograms (f-j) with fitted Gaussians. Different distances were generated by the seeding process described in the text. Pt particles in (a) were fabricated using the seed dispersion, whereas the particles in (b-c) were created with particles with diameters increased by seeded emulsion polymerization. (Samples tilted by 30°).

Table S1. Results of the seeded polymerizations and experimental determination of the Pt content by ICP-OE spectrometry. (Supplementary to Figure 1)

Monomer excess [M]/[M$_{\text{seed}}$]	Diameter Theory* / nm	Diameter (REM) / nm	PDI / %	Pt-content / mg/L	Pt-content / % of seed	Pt-content / %of theory**	Pt-content / wt.-%
0 (seed)	132	132±6	4.5	11.747±0.334	100.00	100.0	1.26
1	137	138±6	4.3	16.295±0.364	94.21	107.2	1.18
2	164	137±5	3.6	15.921±0.446	92.43	102.9	1.16
3	184	137±5	3.6	14.261±0.556	94.36	105.1	1.18
4	201	150±5	3.3	9.015±0.114	64.94	94.9	0.81
5	215	157±7	4.5	8.834±0.238	60.43	101.3	0.76
6	228	193±6	3.1	4.351±0.027	41.68	103.5	0.42
7	239	197±11	5.6	3.157±0.073	26.38	87.3	0.33
8	249	202±8	4.0	2.586±0.082	31.81	113.6	0.38
9	259	218±6	2.8	1.688±0.099	20.51	92.0	0.32
10	267	228±7	3.1	2.460±0.090	19.31	99.1	0.24
11	276	229±9	3.9	1.995±0.094	20.84	108.4	0.27
12	284	254±10	3.9	2.569±0.118	15.76	111.9	0.16

*calculated with 80% conversion

**to calculate the theoretical amount of platinum for the seeded particles, the Pt content of the seed particles determined by ICP was set to 100%; the actual encapsulation efficiency was 66.1 %.

Table S2: Results of the diameters measured from SEM images after deposition of the colloids on the substrate D_{initial}, after the oxygen plasma treatment $D_{60\text{min}}$ as well as after the annealing procedure $D_{1100\,°\text{C}}$. $D_{\text{theo,ICP}}$ shows the theoretical value with respect to the Pt-loading of the PS-spheres.

	D_{initial} / nm	D_{60min} / nm	$D_{1100°\text{C}}$ / nm	$D_{\text{theo,ICP}}$ / nm
Variation of Pt - NP diameter at constant separation distance	175±7	27±2	8±1	10
	196±5	41±3	12±1	14
	185±5	45±2	15±1	16
Variation of Pt - NP separation distance at constant diameter	132±6	32±3	9±1	11
	167±6	35±4	9±1	11
	193±6	37±3	9±1	11
	228±7	36±4	9±1	11
	254±10	39±4	9±1	11