

Editorial Manager(tm) for Journal of Nanoparticle Research
Manuscript Draft

Manuscript Number:

Title: Preparation of size-tunable, highly monodisperse PVP-protected Pt-nanoparticles by seed-mediated growth

Article Type: Brief Communication

Section/Category:

Keywords: platinum; nanoparticle; synthesis; size-control; shape-control; poly-N-Vinylpyrrolidone (PVP); polyol method; seed; growth; catalysis

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Manuscript Region of Origin:

Abstract: We demonstrate a preparative method which produces highly-monodisperse Pt-nanoparticles of tunable size without the external addition of seed particles. Hexachloroplatinic acid is dosed slowly to an ethylene glycol solution at 120 °C and reduced in the presence of a stabilizing polymer poly-N-vinylpyrrolidone (PVP). Slow addition of the Pt-salt first will first lead to the formation of nuclei (seeds) which then grow further to produce larger particles of any desired size between 3 and 8nm. The amount of added hexachloroplatinic acid precursor controls the size of the final nanoparticle product. TEM was used to determine size and morphology and to confirm the crystalline nature of the nanoparticles. Good reproducibility of the technique was demonstrated. Above 7nm, the particle shape and morphology changes suddenly indicating a change in the deposition selectivity of the Pt-precursor from (100) towards (111) crystal faces and breaking up of larger particles into smaller entities.

Preparation of size-tunable, highly monodisperse PVP-protected Pt-nanoparticles by seed-mediated growth

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ABSTRACT: We demonstrate a preparative method which produces highly-monodisperse Pt-nanoparticles of tunable size without the external addition of seed particles. Hexachloroplatinic acid is dosed slowly to an ethylene glycol solution at 120 °C and reduced in the presence of a stabilizing polymer poly-N-vinylpyrrolidone (PVP). Slow addition of the Pt-salt first will first lead to the formation of nuclei (seeds) which then grow further to produce larger particles of any desired size between 3 and 8nm. The amount of added hexachloroplatinic acid precursor controls the size of the final nanoparticle product. TEM was used to determine size and morphology and to confirm the crystalline nature of the nanoparticles. Good reproducibility of the technique was demonstrated. Above 7nm, the particle shape and morphology changes suddenly indicating a change in the deposition selectivity of the Pt-precursor from (100) towards (111) crystal faces and breaking up of larger particles into smaller entities.

KEYWORDS: platinum, nanoparticle, synthesis, size-control, shape-control, poly-N-Vinylpyrrolidone (PVP), polyol method, seed, growth, catalysis

The controlled manufacture of nanoscale building blocks such as nanoparticles¹ and nanowires² has propelled nanotechnology into one of today's most promising and popular fields of scientific research. Future advances require the ability to fabricate building blocks of nanometric dimensions in a reproducible and controlled fashion³. Nanomaterials in the 1-10nm size regime are of particular interest as Raman⁴ & Fluorescence⁵ enhancers and for catalysis applications^{6,7}. Nanomaterials in the 1-10nm size regime are of particular interest because of the gradual transition from single-molecule to bulk-like materials and the changes in electronic, optical and structural properties associated with such a transition. Both, catalytic activity⁸ and selectivity⁹ are known to be influenced by the size of catalytically active noble metal nanoparticles. Therefore, a series of differently sized particles of consummate monodispersity are necessary to elucidate size and shape effects in catalysis. Despite a large choice of synthetic methods published in the literature which produce platinum metal nanoparticles of decent monodispersity and relatively uniform shape, most common techniques are either limited to a single particle size¹⁰ or a narrow size-range¹¹ for which the growth conditions have been optimized. Even nowadays, a significant fraction of newly published preparation techniques produce polydisperse samples¹². Until now, only few catalytic studies dealing with size-dependent activity of Pt-nanoparticles have been carried out, partly because of the lack of a "universal" synthetic method which can cover an entire range of particle sizes of interest. Rioux et al. for example used five differently prepared Pt-nanoparticle samples (solvent, temperature, precursor concentrations etc.) to perform a size-dependent catalytic study on the hydrogenation of ethylene with nanoparticle model catalysts⁸. Ideally, only materials obtained by one and the same synthetic method should be used to perform such a task, because they can guarantee a similar chemical "history". In this letter we demonstrate a novel route to monodisperse PVP-capped Pt-nanoparticles of tunable size in the 3-8nm range.

Figure 1

The schematic shown in Figure 1 illustrates the principle of the seeded growth method. Reduction of the hexachloroplatinic acid (H_2PtCl_6) precursor yields atomic Pt⁰ and small metallic clusters which condensate to form larger clusters or small nanoparticle seeds. A seed particle formed in this way typically consists of a few tens to a few hundred metal

atoms. Such seeds catalyze the reduction of additional precursor material at the interface between the particle and liquid solution. This means that the reduction of H_2PtCl_6 monomer now occurs preferentially on an existing nanoparticle seed rather than in solution. The selectivity of nucleation versus growth reactions depends strongly on the solution concentration of the Pt salt: At high precursor concentrations, condensation of reduced Pt atoms leads to the formation of small clusters. The collision frequency of individual Pt atoms or very small clusters is large due to their statistical abundance and hence, nucleation is preferred.

At low precursor concentrations on the other hand, the mean free path of atomic Pt or other Pt species such as PtCl_6^{-2} is large and nucleation is disfavored; such species will travel a longer time in solution before they collide and fuse with another reactive species. Jana et al. recently have shown that growth versus nucleation selectivity for Au-nanoparticles synthesized by a seed-mediated growth method depends on the concentration of seeds in solution and also on the speed of addition of the reducing agent¹³. In their study, “large” metal precursor solution concentrations ($\sim 0.1\text{mM}$) were used and the selectivity for seeding or growth respectively was achieved by controlling the speed of the reducing agent addition. In our case, slow addition of the metal precursor leads to controlled deposition of prereduced Pt atoms or, more likely, molecular metal precursor species onto already existing seed particles in solution. Consequently, slow dosing of the metal precursor represents a simple and elegant way to simultaneously control particle growth and the size of the final nanoparticle product. Humphrey et al. recently demonstrated the ability to control the particle size and shape of Rh-nanoparticles grown from cluster seeds by the amount and of metal precursor added and the speed of addition¹⁴. Monodisperse particles were only obtained, when the precursor solution was added slowly (10 mg RhCl_3/hr) whereas rapid addition led to the formation of multipod shapes (160 mg RhCl_3/hr). Evanoff and Chumanov¹⁵ have used a strategy similar to the one presented here to grow silver nanoparticles in aqueous solution by hydrogen reduction: the use of silver oxide as the metal precursor, permitted the growth nanoparticles in a controlled fashion to any desired size between 15 and 200nm by simply varying the reaction time. Similar to our experiments, the metal precursor concentration was kept low at all times, limited by the minute solubility of Ag_2O in aqueous solutions, thus favoring growth of already existing particles over nucleation. In this letter we demonstrate the ability to produce monodisperse particles of tunable size in the 3-8nm range by a seed mediated growth technique with in-situ generated seed particles. The

work described here is limited to experiments done in ethylene glycol as a solvent / reducing agent system. Additional experiments were also carried out in aqueous solution with hydrogen as a reducing agent. The reader is referred to the supplemental information for a selection of results on hydrogen reduction seeded growth experiments.

To a stirred 10ml aliquot of ethylene glycol at 120°C was added a small amount (50 μ l) of 1M aqueous sodium hydroxide solution to promote nucleation¹⁶. To this, a solution of hexachloroplatinic acid (5.3mM / 20mg) and PVP (91mM based on VP monomer) in a 9:1 per volume EG/water mixture was dosed slowly (typical rates = 0.5 – 2.0ml / hr) with a mechanical syringe pump and fed to the reaction mixture by means of a capillary (150 μ m bore diameter). Approximately five minutes after dosing the precursor/capping agent solution, a light brown coloration was observed indicating the formation of nanoparticle seeds. With time, the solution became increasingly darker and the final tint was given by the total amount of precursor solution added. After the dosing was complete, the reaction mixture was stirred for an additional 15 minutes and then cooled to room temperature. The nanoparticles were isolated by addition of acetone (approximately three times the reaction volume), subsequent centrifugation and redissolution into ethanol. Samples were analyzed by means of a Philips Tecnai 12 Transmission Electron Microscope at an acceleration voltage of 120kV. Size distribution histograms were obtained from image analysis (200 randomly chosen particles counted per sample).

Figure 2

The size of the particles shown in the TEM images in Figure 2 increases with the total amount of hexachloroplatinic acid precursor added. During an initial study, four different sizes A) through D) of nanoparticles between 3.1 and 7.8nm were synthesized. A repeat experiment (sample E)) was also conducted.

Table 1 shows the results in more detail:

Table 1

All four samples exhibit excellent size monodispersity with typical standard deviations around 15%. Sample C) (20mg added) is the most monodisperse (11.5%) of this first series and also shows the most clearly defined particle shape with predominantly cubic {100} and some tetrahedral-like {111} particles. For very large amounts of H_2PtCl_6 (sample D) added, the particles tend to develop into dendritic rather than tetrahedral-like or cubic shapes, the size-dispersity increases and the average size drops below the value expected from seeded growth (see Figure 3). Although this trend is not completely understood, the results are similar to the findings of Humphrey et al., where particles above 7 nm became more and more dendritic, displaying unusually large size distributions and shape anisotropies¹⁴. More recently, Stoeva et al. have observed a reversible shape and size transformation of Au-nanoparticles at low temperature which is controlled exclusively by action of surfactant and polymer capping agents. A deviation from ideal growth behavior of the largest particles (sample D) is also seen in the size correlation plot shown in Figure 3:

Figure 3

The size correlation plot shows the mean particle diameter d cubed plotted against the amount of hexachloroplatinic acid added. From a geometric consideration it is apparent that the volume of a single nanoparticle is proportional to d^3 . The fact that we observe a linear relationship between the total amount of added Pt and d^3 suggests that Pt is used exclusively for particle growth. This is true for samples A), B), C), and E) (repeat experiment shown below) i.e. for particle sizes smaller than 7nm. If additional seeding or breakup of larger particles were to occur during the growth stage, the average size would drop resulting in a reduced average particle size and hence a deviation from the linear dependence shown in the size correlation plot. Such a deviation is observed in the case of sample D (7.81nm) and is consistent with the poor monodispersity.

In a second experiment, a group of students was asked to reproduce the optimized experimental procedure and to synthesize 6nm Pt-nanoparticles by dosing H_2PtCl_6 / PVP to EG as described above. For this experiment, a larger bore stainless steel syringe (approximately 500 μm inner diameter) instead of a capillary was used. Again, a continuous darkening of the initially colorless solution was observed over the course of the addition of 20mg of hexachloroplatinic acid. The product was recovered as previously described,

suspended into ethanol and analyzed on a Philips CM30 HRTEM at 300kV acceleration voltage. Analysis of the repeat experiment sample E) confirmed a particle size nearly identical (6.23nm) with the original sample C) and even better monodispersity ($\pm 0.45\text{nm}$ or $\pm 9.1\%$) as shown in Figure 4. The latter could be attributed in part to the superior instrument resolution (sharper particle edges) of the CM30 TEM over the previously used Tecnai 12. The crystalline nature of the nanoparticles was confirmed based on three counts of evidence: First, the lattice planes (distance approximately 2.7\AA) are visible in the High-Res TEM image, second, the lattice planes extend over the entire particle and third, the diffraction image shows sharp diffraction spots.

Figure 4

The shape-preference for cubic particles of sample E) shown in Figure 4 is less pronounced than in the case of the original sample C). It is known that both organic (polymers, surfactant molecules) and inorganic compounds (metal ions, electron-donor ligands) can adsorb preferentially adsorb to a certain crystal face of a growing nanoparticle and control its final shape¹⁷. Contamination of the growth solution is the most plausible explanation for the observed shape discrepancy. Dissolved metal ions from the stainless steel syringe-needle (visually corroded after the experiment) are the most likely source of contamination. The different commercial source of the PVP stabilizer and H_2PtCl_6 may also have influenced the experiment. Sensitivity to contamination and shape-directing effects will be the focus of a future study.

The current size-limitation for monodisperse particles of 7nm is also intimately connected with the particle shape: Above that critical size, the Pt-deposition rates onto different faces seems to change suddenly. Closer inspection of the TEM image of sample D) in Figure 2 reveals the parallel existence of two types of differently grown particles: particles of tetrahedral-like $\{111\}$ and cubic crystallographic shapes $\{100\}$ respectively. In sample C) we observe mostly cubic particles and almost no “tetrahedral” ones but in sample D) a significant fraction is $\{111\}$ and $\{100\}$ particles seem less abundant. Therefore a transformation is taking place which converts $\{100\}$ shapes into $\{111\}$. This process is gradual and many odd, intermediate “frozen-in” shapes between the two are visible in the TEM image. A reasonable explanation to account for the observed transformation is a kinetically controlled change in deposition selectivity of Pt from (100) towards (111) crystal

faces favoring the formation of tetrahedral-like particles. In addition, the deposition of Pt onto corners and edges of already existing particles seems preferred which is commensurate with the needle like protrusions seen in the TEM images in Figure 2 (sample D) circled in red. Alternatively the odd particle shapes could be explained by a breaking up of nanoparticles into smaller entities as suggested by the size correlation plot in Figure 3. Despite the lack of a clear explanation for this morphology “phase-transition” at around 7nm the gradual decrease in pH value over the course of the reaction (for each Pt which is deposited, 6 molecules of HCl are formed) could play an important role. Caswell et al.¹⁸ have shown that the hydroxide concentration strongly influences the shape of silver nanostructure growth. Tiny amounts of NaOH favor the formation of nanowires whereas larger amounts of NaOH yield nanorods of short aspect ratio and irregularly shaped nanoparticles. Those observations were explained by a difference in coordination strength of the citrate capping ligand as a result of deprotonation. Wang et al.¹⁹ have studied the direct influence of the pH on the shape of Au-nanorods from seed-rods. As the pH was tuned from pH 3.6 to 9.6, rectangles, dogbone shapes and branched multipods were formed. Another factor which affects the particle morphology is the PVP stabilizer: it is dosed together with the Pt precursor and hence, the PVP solution concentration in the reaction mixture continually increases over the course of the reaction. It is well known, that the shape of nanomaterials depends strongly on the solution concentration of polymeric capping agents²⁰. Secondly, under the given reaction conditions, the PVP stabilizer may decompose partly to produce shorter polymer chains whose adsorption and capping characteristics may differ from the original material. Last but not least, breakup of larger nanoparticles and possibly competitive Ostwald ripening could be responsible for the observed shape change. The longer reaction time at 120°C would favor digestive processes of that nature.

A more detailed understanding of the observed morphology “phase-transition” could bring about an improved synthetic procedure resulting in precise control over particle size and shape over an extended range of particle sizes. This would constitute an achievement of tremendous impact on nanotechnology.

CONCLUSION: We demonstrate here a very promising, generally applicable synthetic scheme to fabricate noble metal nanoparticles by means of the seeded growth method. Using PVP as a stabilizer one is able to obtain monodisperse Pt-nanoparticles of tuneable

size over the range from 3 to 8 nm by simply varying the amount of precursor added. Contingent upon optimization of the synthetic procedure, there is room to extend the particle size range even further. Some of the key advantages of this technique are the inherent simplicity and its potential applicability to other noble metal / stabilizer combinations. The synthesis of core-shell bimetallic nanoparticles is probably the best-known application of the seeded-growth technique²¹. The procedure demonstrated here could be used to produce highly monodisperse core-shell particles of precisely controlled shape.

Acknowledgements: This work was supported by the Swiss National Science Foundation (SNF) and the Director, Office of Science, Office of Basic Energy Sciences, Division of Chemical Sciences, Geological and Biosciences of the U. S. Department of Energy under Contract DE-AC02-05CH11231. We would like to thank Dr. S. Brunner, Pitt Allmendinger and Manuel Hofer from the Zürich University of Applied Sciences, Winterthur for carrying out the reproducibility test experiment. We also thank Dr. Christian Soltmann for assistance with the CM30 Transmission Electron Microscope and Michael Foxe for support with the initial hydrogen reduction experiments.

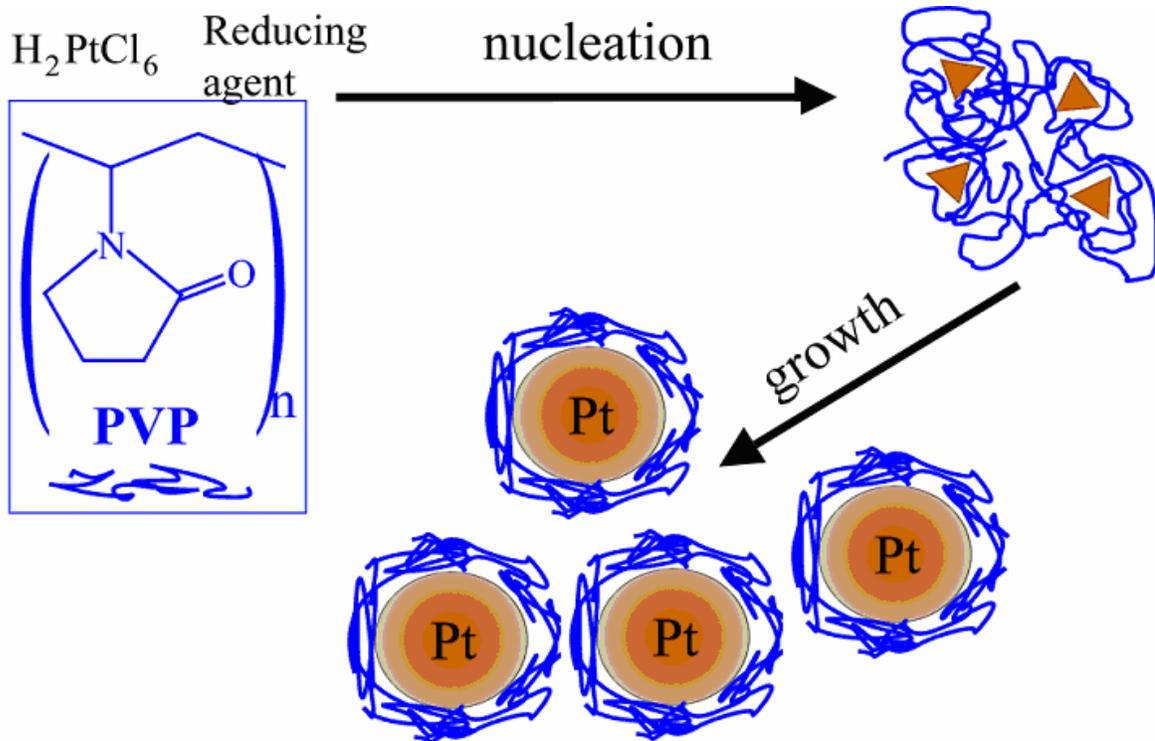
FIGURES and CAPTIONS

Figure 1. Schematic of the employed synthetic scheme: First (nucleation stage), seed particles are formed which are then grown to any desired size during the growth stage.

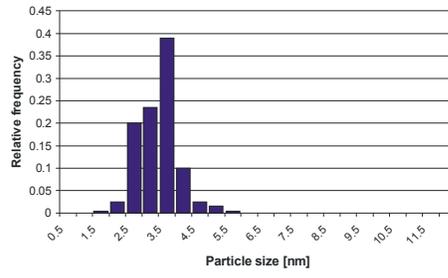
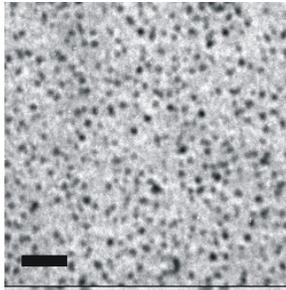
Figure 2. TEM images of four discrete sizes of nanoparticles obtained by the seeded growth technique with increasing amounts of H_2PtCl_6 precursor added. A) 3.1nm, 5mg B) 4.7nm, 10mg C) 6.1nm, 20mg D) 7.8nm, 50mg (scale bar = 20nm)

Figure 3. Size correlation plot showing a linear dependence between the mean particle size cubed (proportional to the particle volume) and the amount of Pt-precursor added. This is strong evidence for controlled particle growth. Sample D) (7.81nm) is not monodisperse and does not follow the same behavior.

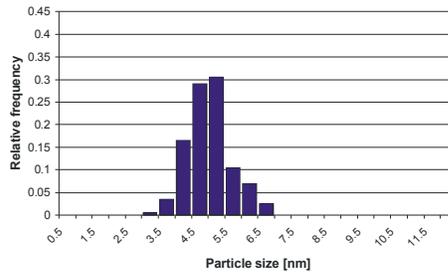
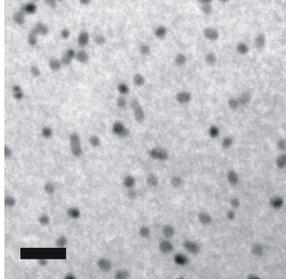
Figure 4. TEM images of 6.1nm nanoparticles (Sample E), 20mg H_2PtCl_6 added) obtained by reproducing the procedure which yielded sample C) shown in Figure 2. Left: overview, scale bar = 20nm. Right: High Resolution image, scale bar = 2nm



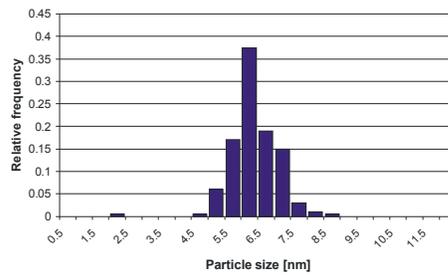
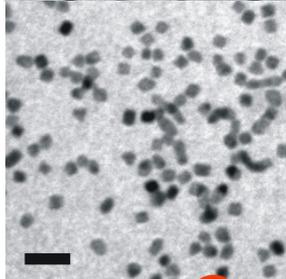
A)



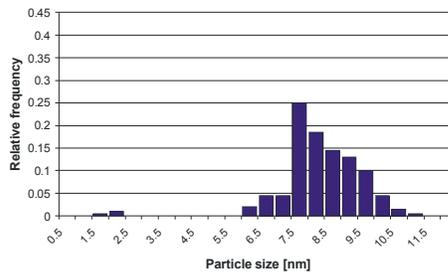
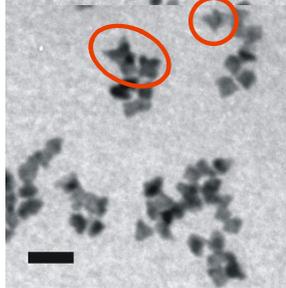
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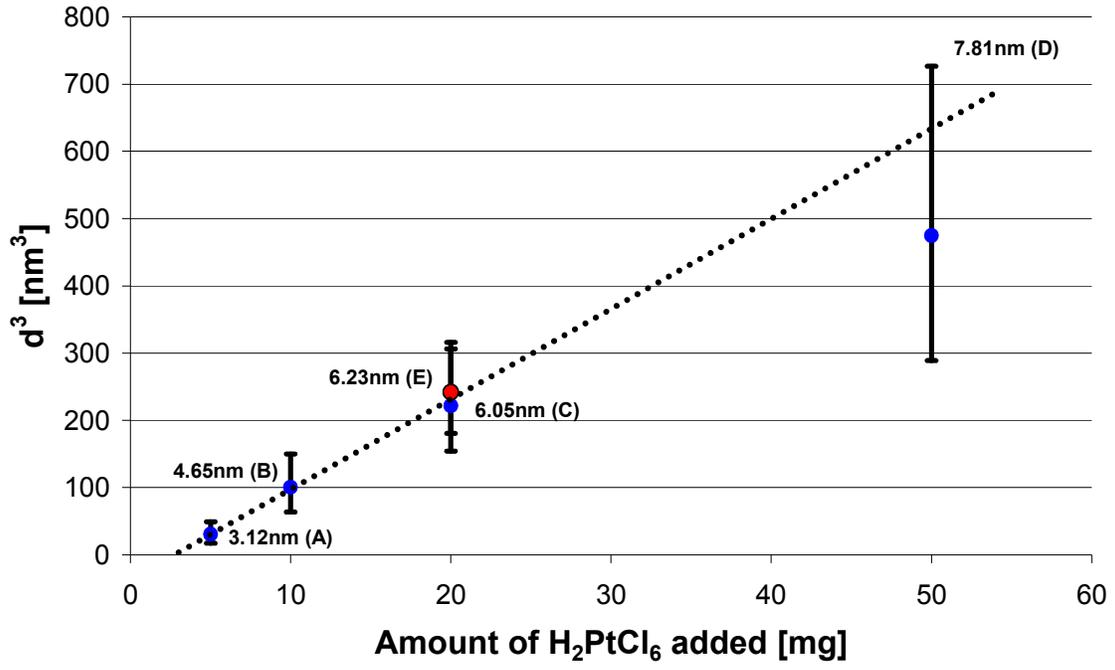
C)



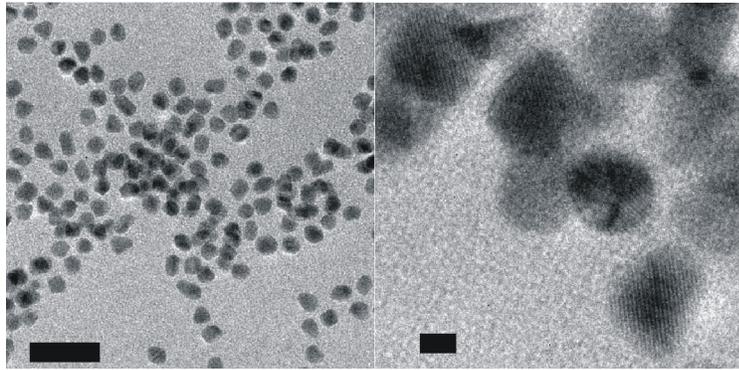
D)



Size correlation plot



E)



TABLES.

Table 1. Summary of seeded growth experiments producing highly monodisperse Pt-nanoparticles of tunable size

Sample	H ₂ PtCl ₆ amount	Avg. size [nm]	Std. deviation [nm]	Std. deviation [%]
A)	5 mg	3.12	0.54	17.4
B)	10 mg	4.65	0.66	14.2
C)	20 mg	6.05	0.69	11.5
D)	50 mg	7.81	1.19	15.3
E)	20 mg (repeat)	6.23	0.58	9.3

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