Preparation of Dispersed Spherical Platinum Particles with Controlled Size and Internal Structure

Versatile and cost-effective route to platinum powders for large scale electronic applications

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Uniform dispersed spherical platinum particles were precipitated by reducing Pt(IV) hexaammine ($[Pt(NH_3)_6]^{4+}$) complex ions with L-ascorbic acid in the presence of polymeric dispersants. By varying the nature and the amount of dispersing agent the average diameter of the Pt spheres could be adjusted between 200 nm and 800 nm. Electron microscopy and X-ray diffraction (XRD) evaluations revealed that the final Pt particles were the result of an irreversible aggregation of small (~6 nm) nanoparticles. The size of the constituent crystallites was controllably increased through a subsequent heat treatment process without affecting the shape or the dispersion of the Pt spheres. The method described represents a versatile and cost-effective route for producing Pt powders at the sub-micrometre or micrometre scale with controlled crystallinity for thick film electronic applications.

Introduction

The optical (1), catalytic (2) and adsorptive (3, 4) properties of dispersed matter depend not only on their chemical composition but also on the size, shape and structure of individual particles (5–7). In most applications, particle uniformity is also essential for optimal performance (5, 8–11). For example, highly uniform Pt particles with different sizes and structures are the preferred choice in electronic (10), catalytic (8, 12, 13) and biomedical (11) applications. The most widely used route to prepare such Pt powders is the liquid phase reduction of Pt salts (14, 15). The primary reasons for the popularity of this approach are the simplicity of the experimental setups and the versatility provided by the variety of solvents, dispersants, complexing agents and reductants used. The selection of the latter is particularly important as it offers the possibility of controlling the reaction kinetics and, implicitly, the properties of precipitated

particles (16). Sodium citrate (17, 18), hydrazine (19) and ascorbic acid (20–26) are often used for this purpose.

While the solution reduction route typically yields uniform and well dispersed single Pt crystals (14, 27), their size is usually very small (less than 10 nm). This is the reason why for applications requiring large Pt crystals (> 1 μm), as is the case of the manufacture of electrodes (28), the Czochralski (29, 30), zone melting (31), or Clavilier (32) methods are preferred (33) despite their poor control of particle size, uniformity, and dispersion. Chemical precipitation methods can also generate sub-micrometre and micrometre size Pt particles under carefully controlled experimental conditions. As a rule, however, they are highly polycrystalline (i.e. formed by aggregation of small nanosize crystallites) (7, 34) and are seldom suitable for electronic applications. The main reason is the overlap of 'intraparticle' sintering of constituent crystallites with the 'interparticle' mass transport during densification, which leads to electrode defects. Gases resulting from the decomposition of organics trapped in the grain boundaries further compromise the quality of the sintered metallic structures and their adhesion to the substrate. In order to extend the range of their applications, the crystallinity of the precipitated particles needs to be increased.

In this study we show that precipitated polycrystalline Pt spheres can be subjected to a heat treatment process that increases their crystallinity and eliminates the undesired residual organics without causing irreversible particle aggregation. The resulting powders possess all attributes (uniformity, dispersion, purity, and structure) necessary for obtaining the thin and dense Pt sintered structures sought in most electronic applications.

Experimental
Materials and Reagents

Hexachloroplatinic acid (H_2PtCl_6) solution containing 25.6 wt% Pt, ammonium hydroxide (NH_4OH) 14.8 N, hydrochloric acid 12.1 N, gum arabic and L-ascorbic acid ($C_6H_8O_6$) reagent grade were all used as received.

Particles Precipitation and Heat Treatment

All precipitation experiments were carried out in a 1 l jacketed glass reactor connected to a constant temperature bath. In the first step, dispersed hexamine Pt complex particles were prepared by delivering over 20 min 24.4 g of concentrated NH_4OH into a stirred H_2PtCl_6 solution. The latter was prepared in the reaction vessel by adding 30.5 g of concentrated H_2PtCl_6 (equivalent to 7.8 g Pt metal) into 275 cm^3 of deionised water in which various dispersants (see **Table I**) were previously dissolved for at least 1 hour. Once the addition of ammonia solution was finished, 27.5 g of L-ascorbic acid crystals were rapidly added to the vigorously stirred Pt complex and the temperature was increased to 68ºC. After maintaining the dispersion at this temperature for 30 min, the polymeric dispersant was hydrolysed to allow the settling and separation of Pt particles. For this purpose, the temperature and pH of the dispersion were adjusted to 83 ± 2ºC and 0.6 ± 0.1 (using concentrated hydrochloric acid solution), respectively, and the stirring was continued for a further 90 min. After settling, the particles were washed several times with deionised water and rinsed with acetone before they were dried at 60ºC in vacuum for 6 h.

Table I gives the nature and the amount of polymeric dispersant used along with the key data for the Pt particles obtained, while **Figure 1** illustrates schematically the precipitation process. The

Table I

Precipitation Conditions and Properties of Precipitated Platinum Spheres

Sample	Dispersing agent	Amount of dispersant, wt% based on Pt	Particle size, nm	Surface area, m^2 g^{-1}	Weight loss, wt%	Crystallite size, nm
S1	Gum arabic	10	550 ± 70	0.4	2.3	6.0 ± 0.5
S2	Gum arabic	20	220 ± 50	1.12	3.4	6.0 ± 0.5
S3	Sodium alginate	3	820 ±100	0.3	2.9	6.0 ± 0.5

subsequent heat treatment step consisted of keeping the dried and screened powders for variable lengths of time in an inert atmosphere at temperatures of up to 500ºC.

Particle Characterisation

The size and morphology of the metallic particles were assessed by field emission scanning electron microscopy (FESEM) using a JEOL JSM-7400F instrument. ImageJ software (35) was used to determine their size distribution based on the acquired electron micrographs. At least 200 randomly selected particles were measured for this purpose. The crystalline structure of the particles was evaluated by powder XRD with a Bruker AXS D8 FOCUS diffractometer. For the XRD pattern acquisition, the step width and period were 0.01º and 3 s respectively, while the source, sample and detector slits were 2 mm, 0.6 mm and 1 mm. The diffraction patterns obtained were used to calculate the size of the constituent crystallites based on Scherrer's equation (36). (Although this approach to determining the subunit size is not very accurate in absolute terms, it was decided that the significant crystallite size increase (up to an order of magnitude) during heat treatment makes XRD an adequate tool to monitor the change

in powder crystallinity). Thermal gravimetric analysis (TGA) measurements (Perkin Elmer Pyris 1 TGA) were used to estimate the amount of organic matter incorporated into the Pt powders.

Results and Discussions
Precipitation of Platinum Spheres

During the slow addition of ammonium hydroxide (**Figure 1**, Step 2), a yellow precipitate of ammonium hexachloroplatinate was formed, followed by immediate conversion to the bright orange Pt(IV) hexaamine complex. The two consecutive reactions are reflected by Equations (i) and (ii):

$$H_2PtCl_6 + 2NH_4OH \rightarrow [NH_4]_2{}^+[PtCl_6]^{2-} + 2H_2O \quad (i)$$

$$[NH_4]_2{}^+[PtCl_6]^{2-} + 6NH_3 \rightarrow [Pt(NH_3)_6]^{4+} \\ + 2NH_4{}^+ + 6Cl^- \quad (ii)$$
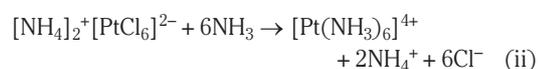
The immediate colour change to green upon the rapid addition of ascorbic acid crystals (Step 4) indicated the reduction of Pt(IV) to Pt(II) and the formation of $[Pt(NH_3)_4][PtCl_4]$ ('Magnus' green salt') a process formally captured by Equation (iii) (36):

$$2[Pt(NH_3)_6]^{4+} + 8Cl^- + 2C_6H_8O_6 \rightarrow [Pt(NH_3)_4][PtCl_4] + \\ 2C_6H_6O_6 + 4NH_4Cl + 4NH_3 \quad (iii)$$
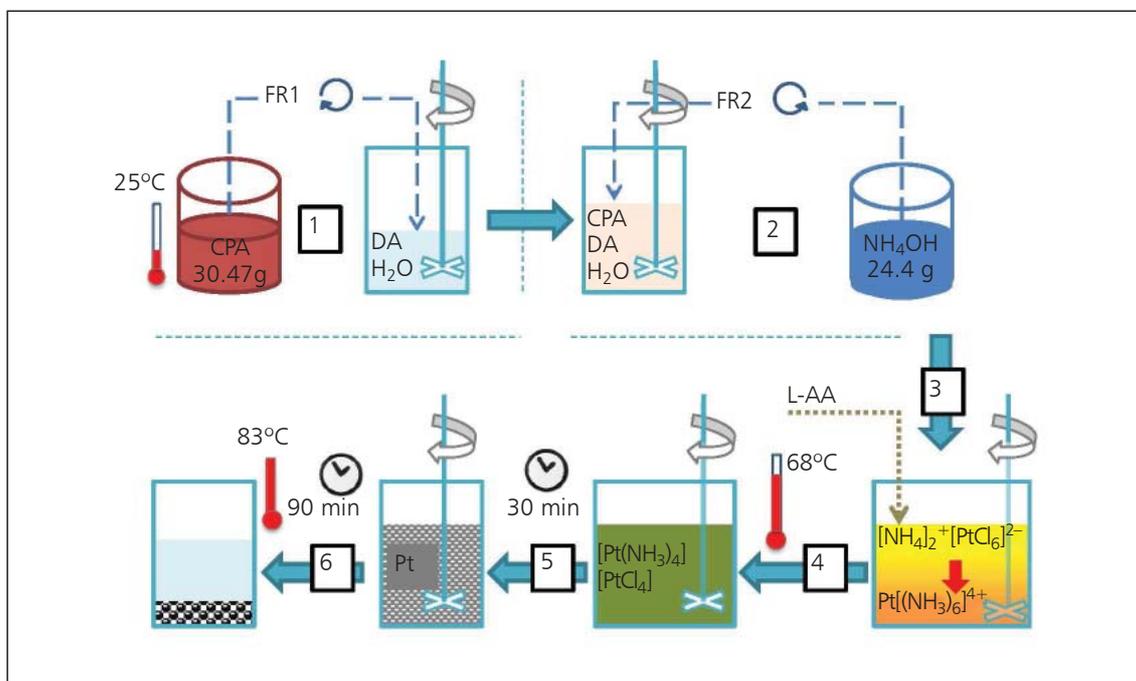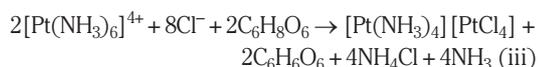
Fig. 1. Schematics of the precipitation process for preparing the spherical platinum particles used in this study. FR (1 and 2) stand for 'flow rate' and indicate pumps used to deliver the reagents in a controlled manner. CPA = hexachloroplatinic acid; L-AA = L-ascorbic acid; DA = dispersing agent

The green precipitate consists of alternately stacked square planar $[PtCl_4]^{2-}$ cations and $[Pt(NH_3)_4]^{2+}$ anions, its formal structure usually being given in a simplified manner as $PtCl_2(NH_3)_2$. At a higher temperature (68ºC), the excess ascorbic acid slowly but quantitatively reduces the Pt^{2+} species to Pt^0 as suggested by the gradual change of the dispersion colour from green to grey-black. This process is formally captured by Equation (iv):

$$PtCl_2(NH_3)_2 + C_6H_8O_6 \rightarrow Pt^0 + C_6H_6O_6 + 2NH_4Cl \quad (iv)$$
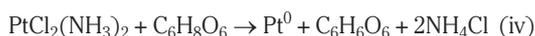
The electron microscopy evaluations of the isolated solids revealed that well dispersed and quite uniform spherical Pt particles were obtained in all experiments (**Figure 2**). The median size of the particles was influenced by both the nature and the amount of dispersing agent used. The average size of the particles decreased from ~550 nm to ~220 nm when the level of gum arabic was increased from 10 wt% to 20 wt% (**Figures 2(a)** and **2(b)**). This outcome is expected as an increased amount of dispersant favours the formation of a larger number of aggregation centres and reduces the number of constituent nanocrystals captured by each aggregate (38). In the case of sodium alginate, when an even lower amount of polymer was used due to a high viscosity of the starting solution,

the average particle size increased to ~800 nm (**Figure 2(c)**).

The X-ray diffractograms of the three samples were essentially indistinguishable. For illustration, the pattern obtained for the particles obtained in the presence of 10% gum arabic is given in **Figure 3(a)**. The unusually broad peaks for such large particles provided the first indication that the metal spheres may be assemblies of much smaller Pt entities. Indeed, the calculations based on Scherrer's equation (36) gave a value of ~6 nm for the size of the Pt crystallites. Additional inspection of the particles at high magnification (**Figure 3(b)**) confirmed both the aggregated nature of the Pt spheres and the calculated size of the constituent crystallites.

Considering the extensive internal grain boundary formed during the aggregation of a very large number of such small entities, it is expected that a significant amount of polymeric dispersant is trapped inside the large spheres. TGA analysis was used to determine not only the total residual amount of organic matter incorporated in the final dry powder but also the dynamics of its decomposition as a function of temperature. The decomposition pattern shown in **Figure 4** for gum arabic was typical for both dispersants but the total weight loss recorded at 450ºC
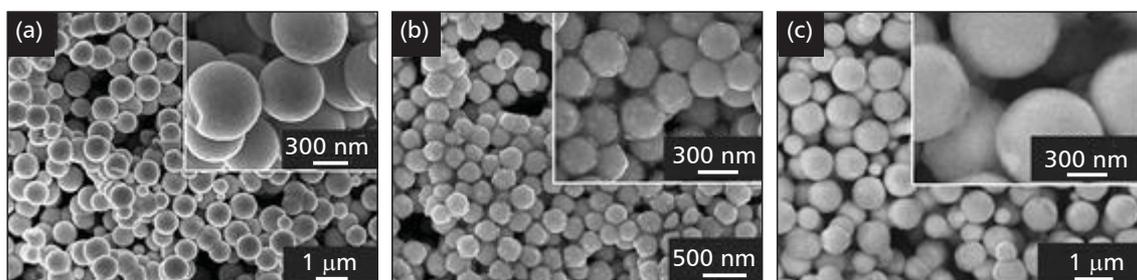
Fig. 2. Field emission electron micrographs of platinum spherical particles obtained in the presence of: (a) 10% gum arabic; (b) 20% gum arabic; and (c) 3% sodium alginate
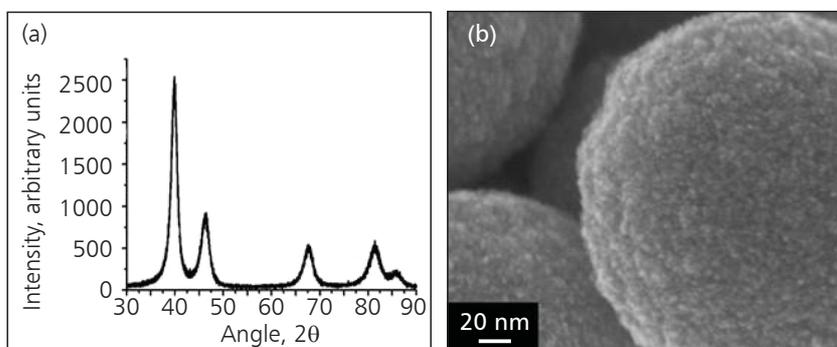
Fig. 3. (a) XRD pattern and (b) high magnification FESEM images of platinum particles in Sample S1

varied with the type and amount of polymer used. In the case of gum arabic, it increased from ~2.3% to ~3.4% when the polymer amount was doubled from 10% to 20% (**Table I**, Samples S1 and S2). The increase in the residual organic matter in the latter case is likely the result of a larger external surface area associated with spheres of smaller diameter. Although the particle diameter was comparable to that recorded in Sample S1, in the case of sodium alginate the weight loss was larger (~2.9 %). Since the internal grain boundary and external surface area in both cases should be roughly similar (comparable size of both crystallites and spheres), the reason for the difference was likely the higher molecular weight of sodium alginate.

Heat Treatment of Platinum Nanoparticles

It is well known that the sintering temperature of nanoparticles is significantly lower than that of much larger entities of the respective materials (39, 40). Since the large precipitated particles contain nanosubunits, finding a temperature where their sintering is confined inside each sphere without intersphere mass transport (and thus powder sintering) taking place could be a viable way to increase particle crystallinity without irreversible particle aggregation. Also, as the sintering temperature of Pt is well above the decomposition point of most organic polymers, another advantage of such treatment would be a significant reduction of the amount of dispersant trapped in the internal grain boundary. In order to find a temperature at which the 'intraparticle' and 'interparticle' sintering are separated, four aliquots of Sample S1 were kept for 1 hour in an inert atmosphere at 200ºC, 300ºC, 400ºC and 500ºC, respectively. XRD analysis revealed a significant increase in the crystallinity of the Pt particles with temperature, as judged both by the width of the diffraction peaks (**Figure 5(a)**) and the increase in the calculated crystallite size (**Figure 5(b)** and **Table II**).
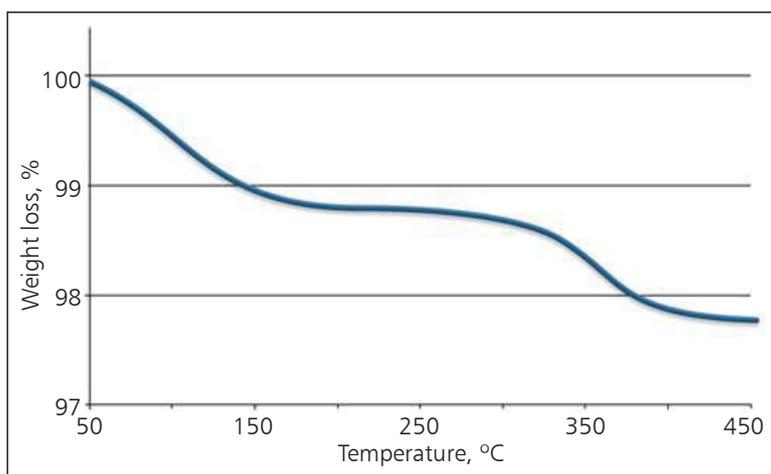
Fig. 4. TGA data for the platinum spheres in Sample S1
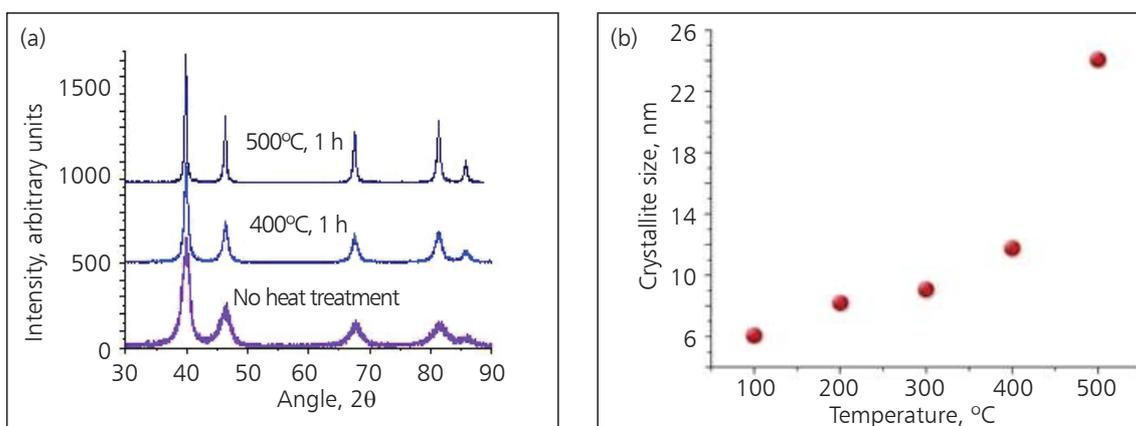
Fig. 5. (a) XRD pattern and (b) calculated crystallite size of platinum spheres as precipitated and treated at different temperatures for 1 hour

Table II

The Variation of Platinum Crystallite Size with Temperature

Temperature, ºC	100	200	300	400	500
Crystallite size (111), nm	6.0 ± 0.7	8.0 ± 0.8	9.5 ± 0.9	12.0 ± 1.2	24.0 ± 2.5

As indicated by the TGA data in **Figure 6**, the increase in crystallinity was also associated with a significant reduction in the amount of residual organic matter (from ~2.3% to ~0.2%).

Compared to the image of the original precipitated particles shown in **Figure 3(b)**, the scanning electron microscopy (SEM) of the heat treated powders (**Figures 7(a)** and **7(b)**) showed a much smoother surface, a clear indication of a significant reduction in the internal grain boundary. It is noteworthy that the exposure to elevated temperature for a relatively long time also causes the merging/sintering to a certain extent of the surface crystallites resulting in the loss of their original morphology. The analysis of multiple micrographs also showed that no interparticle

Fig. 6. TGA plots for precipitated and heat treated platinum powders

'bridging' took place at temperatures of 400ºC or below. In contrast, at 500ºC severe interparticle fusion was observed (**Figure 7(c)**).

These findings suggest two sintering regimes of spherical composite particles taking place at different size scales. At temperatures below 400ºC, 'intraparticle' coarsening occurs as a result of the growth of constituent subunits and the reduction of internal grain boundaries. At 500ºC, interparticle mass transport becomes significant and results not only in the growth of the constituent Pt crystallites, but also severe aggregation of the large Pt spheres. Since the latter cannot be redispersed to form electronic inks capable of depositing smooth and continuous thin Pt films, the optimum temperature at which powders suitable for electronic applications (crystalline and non-aggregated) can be prepared is ~400ºC.

Conclusion

This study describes a precipitation method for obtaining concentrated dispersions of uniform polycrystalline Pt spheres. By tailoring the reaction conditions it is possible to control the final particle size in the 200 nm to 800 nm range. A heat treatment process capable of increasing the crystallinity of the precipitated spheres and decreasing the content of residual dispersant is also reported. The combination of the two processes makes possible the preparation of reasonably crystalline, uniform and well dispersed Pt spheres, which are suitable for thick film electronic applications. The use of widely available Pt salt, common reagents, and the simple experimental
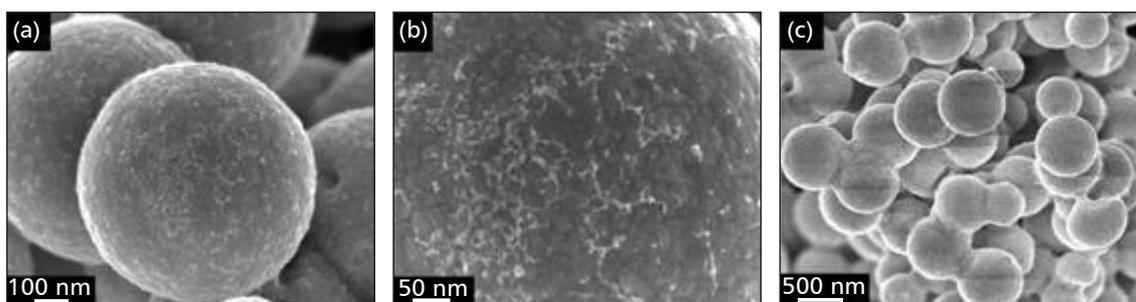
Fig. 7. (a) and (b) FESEM of platinum spheres kept at 400ºC at two magnifications; (c) FESEM of platinum spheres heat treated at 500ºC for 1 hour

setup makes the reported preparation route suitable for the manufacturing of spherical Pt powders on a large scale.

Acknowledgements

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