

Synthesis and Characterization of Small Platinum Particles Formed by the Chemical Reduction of Chloroplatinic Acid*

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The preparation of platinum particles by the chemical reduction of chloroplatinic acid has been investigated in detail. The morphology and size of the product depends on the nature of the reducing agent, the presence and type of protective agent, and the reduction conditions. By carefully controlling these parameters, platinum spheres ($\approx 20\text{--}30$ Å diam), strands (≈ 60 Å diam), and composites ($\approx 100\text{--}200$ Å) can be synthesized. Polyvinylpyrrolidone was found to be the optimum protective agent due to its low protective ratio and high purity. The distribution of particle diameters for the spherical particles can be described by a log-normal distribution function. This work lays the foundation for studies of the chemical and physical properties of these particles. The applicability of this chemical-reduction approach to other systems is also outlined. © 1987 Academic Press, Inc.

Introduction

Fundamental knowledge and understanding of the physical and chemical properties of small metal particles is of considerable scientific as well as technological importance. Their finite dimensions ($\approx 10\text{--}100$ Å) result in an appreciable fraction of the metal atoms residing on the surface, where they can participate directly in catalytic reactions. Hence both surface as well as interior electronic states can contribute to the properties of such particles. Although the surface states are of obvious importance in

catalysis, the interior states, to which the surface states can be coupled, are also of interest, in part because of the expected quantization of energy levels in small metal particles (1-4). One of the central problems in catalysis is to determine the size dependence of the electronic properties of catalysts and to investigate its influence upon catalytic reactions. This problem can be addressed best by studying small, uniform catalyst particles as a function of particle size.

Platinum is an extremely important catalyst (5-7) and a prime candidate to probe the dependence of electronic and catalytic properties on particle size. In this regard, we have shown previously that it is possible to prepare very uniform spherical platinum particles having a mean diameter of 22 ± 4 Å by reducing chloroplatinic acid with so-

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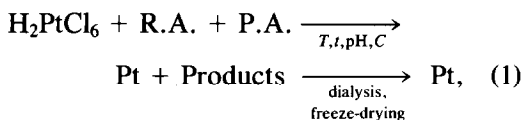
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dium citrate and have obtained the first evidence of quantum-size effects in platinum from magnetic susceptibility measurements on these particles (2). Since this chemical-reduction approach has several advantages over other synthetic techniques, such as evaporation (8), irradiation (9), thermal decomposition (10), and particle-beam (11) methods, in terms of higher yield, narrower size distribution, ability to characterize the particles directly with electron microscopy, and chemical flexibility, we have initiated a program to investigate the synthesis of small platinum particles by chemically reducing chloroplatinic acid. In this study we have extended our previous work by examining in detail the synthesis of small platinum particles by the chemical reduction of chloroplatinic acid using a variety of reducing and protective agents to explore the potential of this method.

Experimental

Our procedure for the aqueous reduction of chloroplatinic acid can be summarized by the following schematic equations:



where R.A. is the reducing agent, P.A. is the protective agent, T is the reaction temperature, t is the reaction time, pH is the negative logarithm of the hydrogen ion concentration, and C is the concentration of reagents. There are two steps in the overall process: (1) production of a platinum hydrosol after reduction, and (2) separation of the platinum particles from the hydrosol. To prevent coagulation of the platinum particles in the hydrosol, they must be protected with an organic protective agent, which is normally added with the reducing agent prior to introduction of the chloro-

platinic acid. In sample preparations a five-fold excess over the minimum protective ratio, i.e., the ratio of the weight of protective agent to the weight of particles protected, was used to ensure adequate protection. Then, as we shall demonstrate below, by carefully controlling the reaction temperature, time, pH, and concentration of reagents, it is possible to grow quite uniform platinum microcrystals in some cases and interesting geometrical arrays in others. Ionic by-products are removed from the hydrosol by dialysis prior to drying the protected particles. The dialysis was performed by placing the hydrosol in three-quarter-inch cellulose dialysis tubing (VWR Scientific, Inc.), which was previously cleaned by dialysis. After addition of the hydrosol, the tubing was tied off at each end and placed in a large bath. The water in this bath was changed until its resistivity reached that of the pure, glass-distilled water initially added to the bath. Freeze-drying was used to remove water and produce the final, concentrated, product because it is a low-temperature technique that minimizes particle sintering. Using this method relatively large amounts of sample can be prepared (50–100 mg) having a large weight percentage of platinum (≈ 50 wt%) and a relatively narrow size distribution using standard, inexpensive equipment. Furthermore, electron microscopy can be used directly to characterize the particles produced by this procedure. For this purpose a JEOL JEM 100B electron microscope was used, and the platinum hydrosol was freeze-dried onto carbon-coated, copper microscope grids to simulate the final product.

This chemical-reduction technique requires considerable care to prepare a high-quality product (12, 13). All glassware must be thoroughly cleaned, and for this purpose a satisfactory cleaning solution can be prepared by mixing 45 ml of 45% HF, 165 ml of concentrated HNO_3 , 200 ml of H_2O , and 10

g of Alconox detergent. The glassware should be rinsed several (≈ 20) times with deionized water followed by several more (≈ 5) rinses with glass-distilled water. All water used in the preparation should be deionized, passed through an organic contaminant filter, and then distilled in a glass still, because impurities in the water can influence the growth and homogeneity of the microcrystals. Stirring of the reaction mixture with an overhead glass propeller-type stirrer is preferred to avoid scratching the glass reaction vessels, since any scratches can provide unwanted nucleation sites. The purest possible reagents should be used in these preparations, and in cases where commercial purity was inadequate, the reagents were further purified in our laboratories.

The chloroplatinic acid was obtained from Gallard-Schlesinger, and was their highest grade, 99.9%. Major impurities (>10 ppm by wt) in a typical lot of H_2PtCl_6 were Fe (191 ppm), Ca (154 ppm), Al (85 ppm), Si (78 ppm), Na (70 ppm), Mg (25 ppm), and Pd (12 ppm). The following primary reducing agents were used: sodium borohydride (Alpha analytical grade, 99.9%); hydroxylamine hydrochloride, $\text{NH}_2\text{OH}\cdot\text{HCl}$ (Fisher, A.C.S. grade); dimethylamine borane, $(\text{CH}_3)_2\text{HNBH}_3$ or DMAB (Chemical Procurement Laboratories). The DMAB was purified by vacuum sublimation at 25°C (14, 15) before use and was collected on a dry ice-acetone cold finger. Other reducing agents employed were sodium citrate, sodium formate, hydrazine monohydrate, trimethylamine borane, sodium trimethoxyborohydride, hydrogen peroxide, formaldehyde, hydroquinone, pyrocatechol, and 2,4-diaminophenol. The primary protective agent employed was polyvinylpyrrolidone, PVP (Sigma; 10,000 mol. wt). Other protective agents used were sodium polyacrylate (Rohm and Haas, GS grade), polyvinyl alcohol (Sigma, type II), and gelatin.

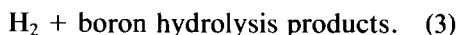
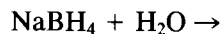
Results and Discussion

I. Syntheses Using NaBH_4

Following the reduction technique of Berry (16), who used NaBH_4 in the preparation of silver microcrystals, NaBH_4 was found to readily reduce H_2PtCl_6 to colloidal platinum. The method involves the rapid addition of a dilute solution of H_2PtCl_6 to a dilute solution of NaBH_4 . Reduction by this procedure is instantaneous. Concentration, temperature, and the method of addition of reactants was optimized to produce the smallest, most homogenous Pt microcrystals possible.

1. *Standard preparation.* In a typical preparation, 8 ml of 0.015 M H_2PtCl_6 was injected rapidly using a syringe into 1 liter of vigorously stirred, ambient-temperature, $6.6 \times 10^{-3}\text{ M}$ NaBH_4 . Prior to the addition of H_2PtCl_6 , the pH of the NaBH_4 solution was adjusted to 12 with NaOH , since NaBH_4 is stable in aqueous solution at a pH of 11 or greater at ambient temperature. The protective agent PVP is not attacked by NaBH_4 , so that a 0.02 g/liter PVP solution was added before the injection of H_2PtCl_6 to produce a fivefold excess of PVP over the minimum protective ratio of 0.13. For future reference, this procedure will be referred to as the standard NaBH_4 preparation.

The probable overall chemical reactions or this preparation are given below:



Once formed, the unprotected platinum microcrystals act as highly active catalysts for the hydrolysis of NaBH_4 (6) via reaction (3), so that a large excess of NaBH_4 is needed to ensure reasonable completion of reaction (2). Below a certain H_2PtCl_6 concentration, reaction (2) is no longer compet-

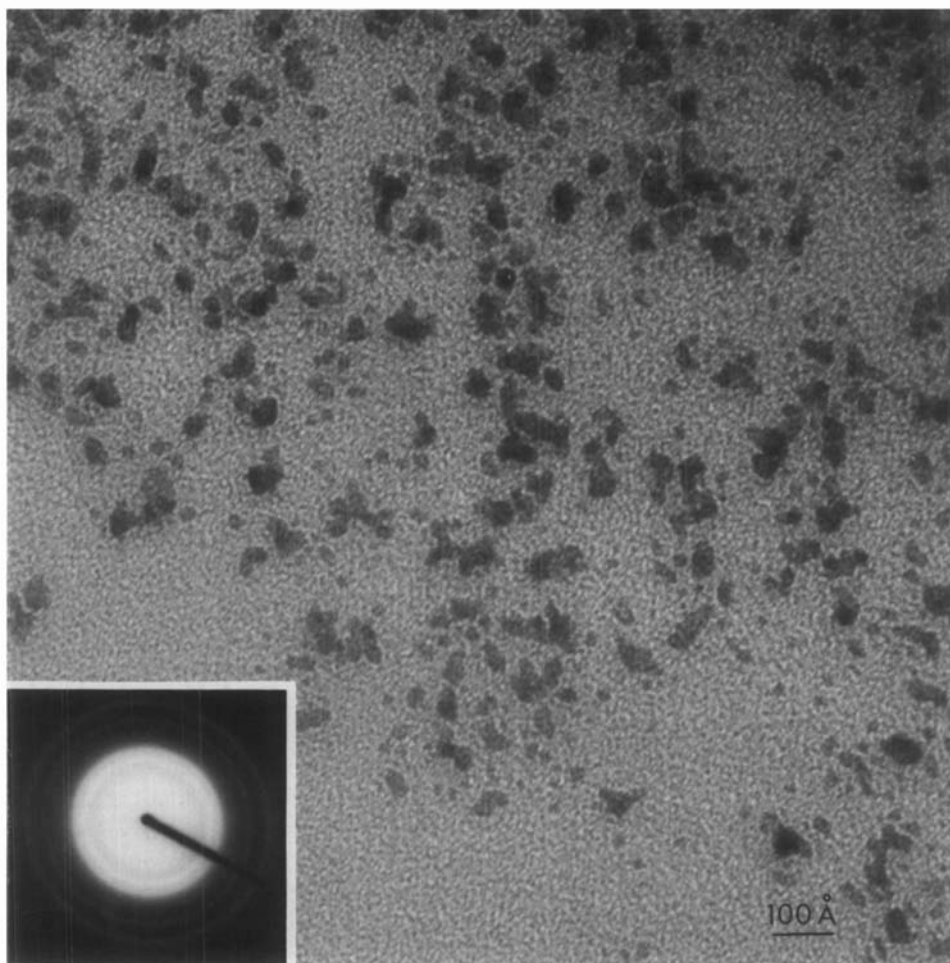


FIG. 1. Electron micrograph of a standard NaBH_4 preparation. The granular background is due to the amorphous carbon-film support. An electron diffraction pattern for the preparation is shown in the lower left corner.

itive with (3), and we have found that a concentration of almost $4.5 \times 10^{-5} M$ H_2PtCl_6 remains after the reduction regardless of the initial H_2PtCl_6 concentration.

Figure 1 shows an electron micrograph of a typical standard NaBH_4 preparation. It is apparent that aggregation of individual particles has occurred to some extent. Both X-ray and electron diffraction patterns were characteristic of platinum. A histogram of the particle-diameter distribution is displayed in Fig. 2. The skewness of the distri-

bution suggests that it may be better described by a log-normal than a Gaussian distribution, as observed for small particles produced by natural processes in soils or rocks, mechanical grinding (17), and evaporation (8). The log-normal distribution is discussed in Section VIII of this paper.

2. *Reverse preparation.* As its name suggests, in this preparation the order of addition of the H_2PtCl_6 and NaBH_4 are reversed, i.e., the NaBH_4 solution is injected into the H_2PtCl_6 solution. Typically, 8 ml of

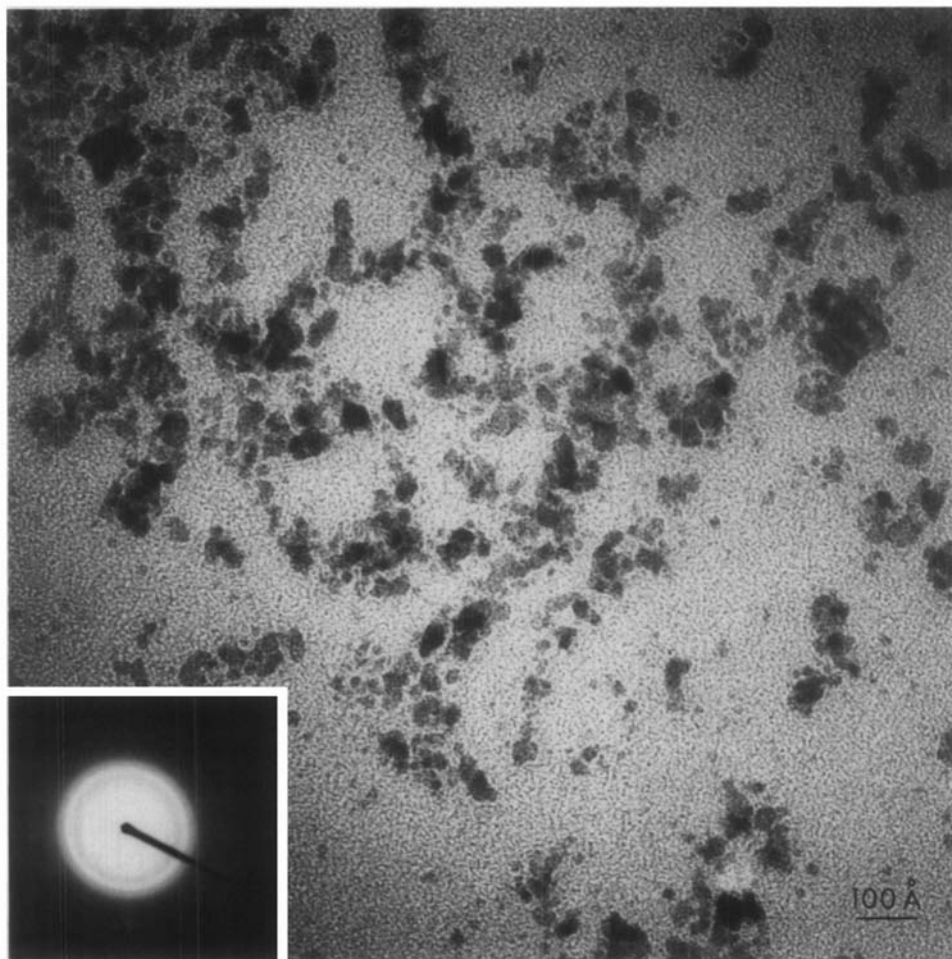


FIG. 3. Electron micrograph of a reverse NaBH_4 preparation. An electron diffraction pattern for the preparation is shown in the lower left corner.

ties is believed to be largely independent of relative supersaturation. In contrast, the rate of homogeneous nucleation, where nucleation occurs because the necessary number of atoms or molecules come together in the proper orientation, increases exponentially with relative supersaturation (21). Due to the extremely low solubility of platinum in water, the relative supersaturation of platinum is high for all concentrations of reduced H_2PtCl_6 present. Our observation that particles of colloidal dimensions are

formed indicates that nucleation is predominant over growth. If the concentration of H_2PtCl_6 is increased, then the relative supersaturation of platinum will change very little, but the proximity of nuclei to unreduced H_2PtCl_6 molecules is greater. Therefore, possibly larger platinum microcrystals can be grown by increasing the initial H_2PtCl_6 concentration.

Since the reaction occurs very rapidly, mixing effects and the instantaneous concentration at injection may be more impor-

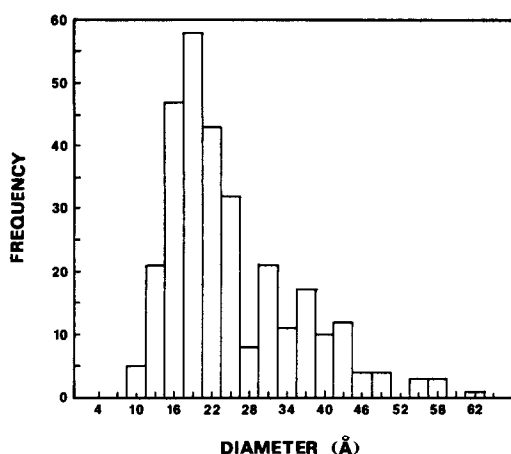


FIG. 4. Histogram of the particle diameters from a reverse NaBH_4 preparation. The sample population was 300. The mean diameter is 25 \AA , the median is 23 \AA , and the standard deviation is 10 \AA .

tant than the overall H_2PtCl_6 concentration after mixing. Two experiments were performed to check the relative importance of these effects. In the first experiment a small amount of very concentrated H_2PtCl_6 , giving the same overall H_2PtCl_6 concentration as a standard NaBH_4 preparation, was injected. Specifically, 0.16 ml of 0.384 M H_2PtCl_6 was injected into 500 ml of standard NaBH_4 reducing solution, whereas in the standard NaBH_4 preparation, 4 ml of 0.015 M H_2PtCl_6 was injected into 500 ml of reducing solution. Electron micrographs showed that larger microcrystals are present ($\approx 50\text{--}60 \text{ \AA}$), but smaller microcrystals ($\approx 20\text{--}30 \text{ \AA}$) are also observable. Close examination of the micrographs reveal that many of the larger microcrystals are actually composed of smaller microcrystals that are sintered together.

In the second experiment, about a four-fold increase in the overall H_2PtCl_6 concentration was achieved using the same stock solution (0.015 M) as the standard NaBH_4 preparation. In this case 15 ml of 0.015 M H_2PtCl_6 was injected into 500 ml of reducing solution, where the ratio of PVP and

NaBH_4 to H_2PtCl_6 was maintained at the same level as in the standard NaBH_4 run. As in the first experiment, larger microcrystals are formed, but it is evident that considerable sintering has occurred. Hence, both experiments yield similar results in the sense that there is an increased tendency for individual microcrystals to sinter together, which strongly suggests that growth via increased H_2PtCl_6 concentrations is due to sintering.

5. *Strand preparation.* To determine the maximum extent of sintering possible, the overall H_2PtCl_6 concentration was increased even further in the absence of PVP. In this preparation, 25 ml of 0.015 M H_2PtCl_6 was pipetted into 475 ml of a stirred, 0.03 M NaBH_4 reducing solution having a pH of 12. An electron micrograph of this preparation is shown in Fig. 6. Remarkably, a chain-like network composed of approximately $60\text{-}\text{\AA}$ -diameter links is observed. For future reference, this preparation will be referred to as the strand preparation.

6. *Diffusion preparations.* Since increasing the H_2PtCl_6 concentration was not a successful approach to producing uniform microcrystals greater than about 30 \AA in size, the question arises as to whether it is

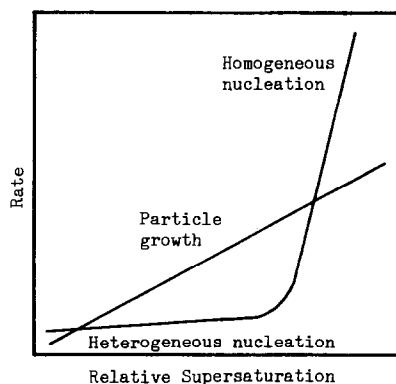


FIG. 5. The dependence of the rates of nucleation and particle growth on relative supersaturation.

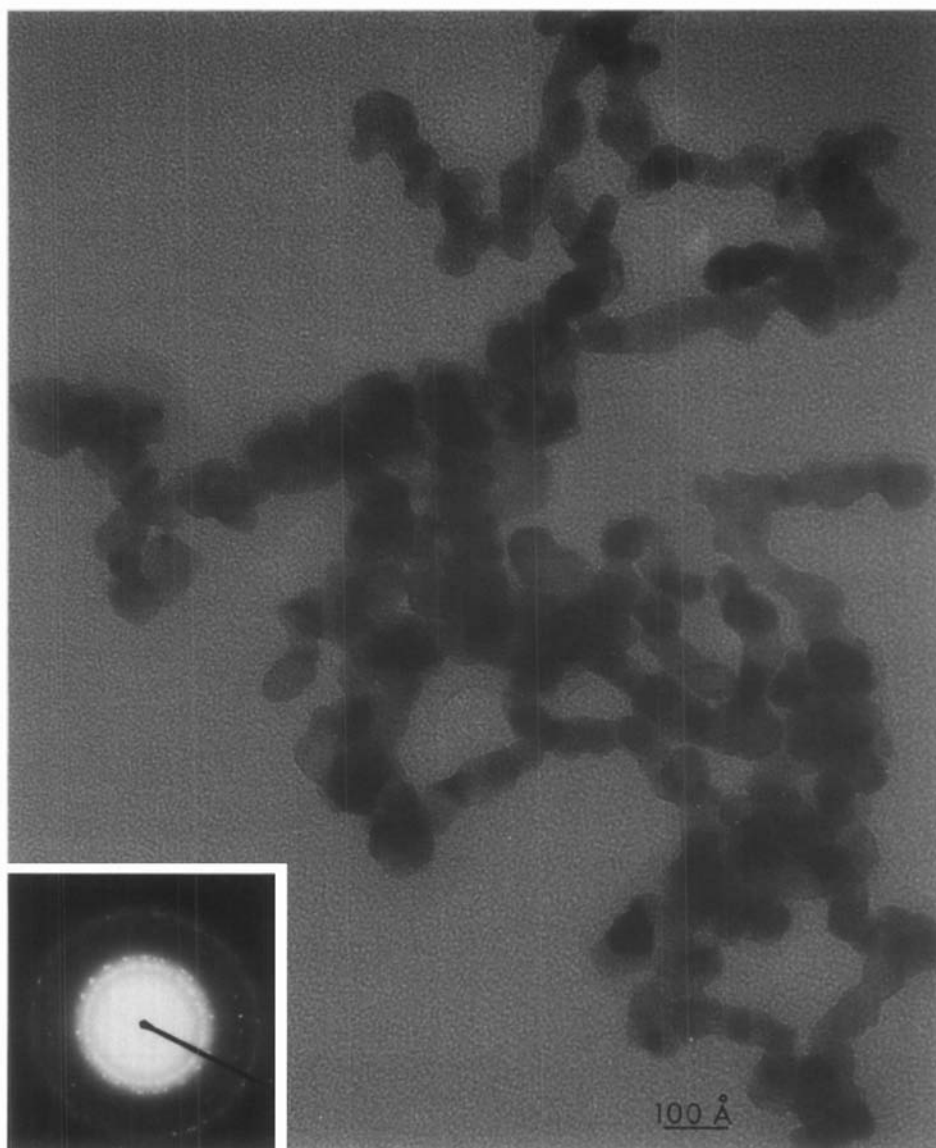


FIG. 6. Electron micrograph of a strand NaBH_4 preparation. An electron diffraction pattern for the preparation is shown in the lower left corner.

possible to prepare smaller microcrystals by keeping the instantaneous concentration of H_2PtCl_6 or NaBH_4 very small. In principle, this can be accomplished by introducing one of the reactants into the reaction medium by diffusion through a semipermeable membrane.

Cellulose dialysis tubing having a pore size of about 20 \AA was used as the diffusion barrier. Diffusion of the large, hydrated H_2PtCl_6 molecule compound to NaBH_4 is negligible. For this reason it is necessary to place the NaBH_4 solution inside the dialysis tubing, which is suspended in a stirred reac-

tion medium containing H_2PtCl_6 , because if H_2PtCl_6 is placed inside the dialysis tubing, then reduction takes place inside the tubing and stirring is impossible. Systematic variation of the H_2PtCl_6 and NaBH_4 concentrations, in addition to a variety of experimental configurations, showed that the reduction process proceeded slower by the diffusion method than by the similar reverse NaBH_4 procedure, but the size of the microcrystals was essentially unchanged (diam $\approx 20\text{--}30 \text{ \AA}$). Hence, nucleation appears to be dominant under the conditions that are possible for reduction in aqueous solutions of H_2PtCl_6 using NaBH_4 as the reducing agent.

7. *Epitaxial preparation.* Nucleation has been favored in all of the above preparations. If larger microcrystals are to be grown, then preference must be shifted from nucleation to growth. A successful approach for gold microcrystals is to start with microcrystal seeds already present in the reaction medium (22). The microcrystal size resulting from this growth process can be described by the equation (22)

$$d = d_0[(m_{\text{Au}} + m_{\text{Cl}})/m_{\text{Au}}]^{1/3}, \quad (5)$$

where d is the final diameter of the gold microcrystals, d_0 is the diameter of the seed crystals, m_{Au} is the mass of the gold present as seeds, and m_{Cl} is the mass of the gold present as gold chloride.

Using Eq. (5), sufficient standard NaBH_4 microcrystalline seeds, unprotected by PVP, were added to a standard NaBH_4 preparation reaction medium to produce 44- \AA microcrystals via an epitaxial process. The procedure for producing standard NaBH_4 microcrystals was then followed, except no PVP was added until the reaction was complete. If added prior to the reaction, PVP might isolate the seed microcrystals and prevent growth. However, no significant change in microcrystal size relative to the standard NaBH_4 preparation was observed.

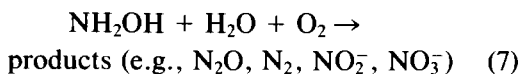
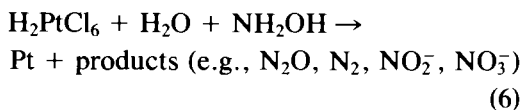
Alternatively, it is possible to produce nuclei *in situ* by taking advantage of the difference in reaction rate for the rapid standard NaBH_4 preparation compared to the rather slow reverse NaBH_4 preparation. Instantaneous nuclei or seeds can be produced by using the standard NaBH_4 procedure in a reverse NaBH_4 reaction medium. The reverse NaBH_4 reaction medium was prepared with and without PVP. Next, NaBH_4 was injected into this medium, initiating the reverse NaBH_4 process. This was followed by the immediate injection of 0.015 M H_2PtCl_6 to produce nuclei for the slower, reverse NaBH_4 process. The amount of H_2PtCl_6 injected was sufficient to produce 60- \AA nuclei according to Eq. (5). However, it was found that the addition of PVP before or after the reaction had little effect on the growth process, and in both cases epitaxial growth failed to occur. In both preparations, 20- to 30- \AA microcrystals were produced with different degrees of sintering. Hence we conclude that even epitaxial-growth methods cannot be used to produce larger homogeneous microcrystals, perhaps due to kinetic factors or possibly contaminants on the surface of nuclei which inhibit growth.

II. Syntheses Using Hydroxylamine Hydrochloride

When hydroxylamine hydrochloride is used to reduce HAuCl_4 , negligible reduction takes place without the presence of gold nuclei (22). Therefore, the hydroxylamine-gold chloride solution is a pure growth medium, and the introduction of gold nuclei into this medium induces instantaneous epitaxial growth. However, in the case of platinum, no immediate reaction occurred with the introduction of standard NaBH_4 microcrystal nuclei into a hydroxylamine-chloroplatinic acid medium. After about 3 days, there were some signs of a hydrosol, but examination of the hydrosol by electron microscopy revealed only 20- to

30-Å microcrystals. Hence, it appears that the hydroxylamine-chloroplatinic acid solution is not a growth medium, but rather a medium for producing 20- to 30-Å platinum microcrystals.

When H_2PtCl_6 is reduced using $\text{NH}_2\text{OH}\cdot\text{HCl}$, a stable hydrosol is not produced and flocculation almost always occurs. Resuspension of the microcrystals using an ultrasonic bath in the presence of PVP resulted in incomplete dispersion. Generally, gross flocculation of a hydrosol is accompanied by large-scale clumping. However, relatively unsintered platinum microcrystals are synthesized using $\text{NH}_2\text{OH}\cdot\text{HCl}$, even though a stable hydrosol is not produced. Feasible reactions for the reduction process are given below:



The concentration of NH_2OH is governed by reaction (8). Hydroxylamine, once formed, is unstable and easily oxidized to a variety of products via reaction (7). Competition between reactions (6) and (7) leads to incomplete reduction of H_2PtCl_6 and problems in reproducibility, especially at elevated temperatures.

Microcrystals were synthesized by separately heating equal volumes of 0.0005 *M* H_2PtCl_6 and 0.0018 *M* $\text{NH}_2\text{OH}\cdot\text{HCl}$ to a particular temperature. These solutions were then mixed, and the reaction was run to completion in a constant-temperature bath. Vessels used at elevated temperatures were fitted with condensers to maintain a constant reaction volume. After completion of the reaction, PVP was added at a concentration of 0.033 g/liter, and by-products were removed by dialysis.

The reaction proceeds through a certain scheme regardless of the temperature. First, yellowish-brown particles are produced and swirl throughout the reaction mixture. These particles gradually turn black over a period of time that increases with decreasing temperature. At a reaction temperature of 90°C, the mixture turned black about 30 min after the reactants were mixed, whereas at 60°C about 3 hr were required to observe the same effect. Electron microscopy revealed that at 90°C substantial clumping of the microcrystals has occurred, whereas at 60°C most of the microcrystals are 20 to 30 Å in size and well separated but there is still some evidence of sintering.

Since sintering is reduced at lower reaction temperatures, the reaction was run at 4°C in a cold room to minimize sintering. The hydroxylamine hydrochloride concentration was increased to 0.006 *M* to reduce the rather long reaction time. After approximately seven weeks, the reaction was judged to be complete, since no further darkening of the reaction was observed. Very uniform, unsintered platinum microcrystals were produced by this procedure, as illustrated by the electron micrograph in Fig. 7 and the particle-size distribution in Fig. 8. For future reference, we shall refer to this procedure as the 4°C $\text{NH}_2\text{OH}\cdot\text{HCl}$ preparation.

III. Syntheses Using Dimethylamine Borane

Dimethylamine borane is used industrially for electrodeless plating. In electrodeless plating, the plating bath is thermodynamically unstable, but kinetically stable, and decomposition of the bath leads to deposition of metal. This process occurs only when the substrate is covered with a certain critical coverage of catalyst which depends on the catalyst used, with typical catalysts being palladium, gold, silver, and copper (23). The similarity between platinum-mi-

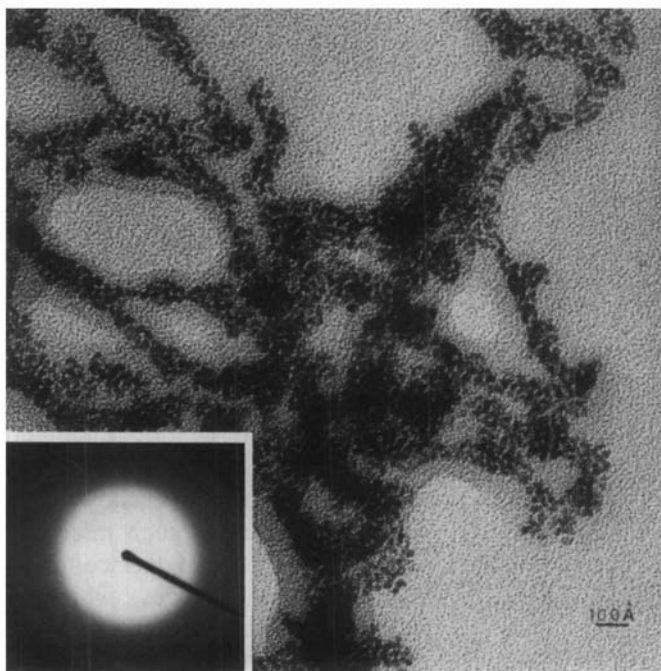
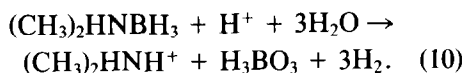
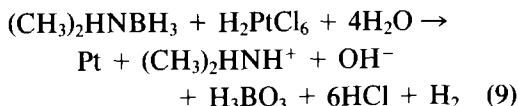


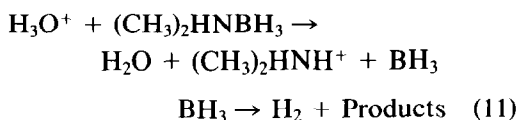
FIG. 7. Electron micrograph of a hydroxylamine hydrochloride preparation (4°C reaction temperature). An electron diffraction pattern for the preparation is shown in the lower left corner.

microcrystal growth and plating on a catalytic site is obvious, so that DMAB is a potential candidate for producing microcrystals larger than 30 Å.

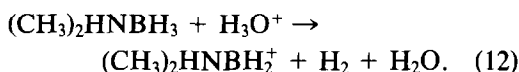
Initial H_2PtCl_6 reduction experiments using DMAB showed a strong dependence on pH and DMAB concentration. If the pH exceeds 12, then the reduction process is severely retarded, and only at very high DMAB concentrations ($\geq 0.1 M$) will reduction occur. The stability of the hydrosol is dependent on the amount of DMAB used in the reduction. Either a reaction by-product or excess DMAB sensitizes the hydrosol, so that flocculation results. At $\text{pH} \leq 10$, essentially 100% of the H_2PtCl_6 is reduced when the molar ratio of DMAB to H_2PtCl_6 is as low as 2.5 to 1, and at this DMAB concentration the hydrosol is not sensitized. The probable overall reactions are summarized below:



Two possible mechanisms (24) have been proposed for reaction (10):



or



The first mechanism involves the displacement of BH_3 by a proton followed by the rapid reaction of BH_3 , whereas the second consists of direct attack on the B-H bond

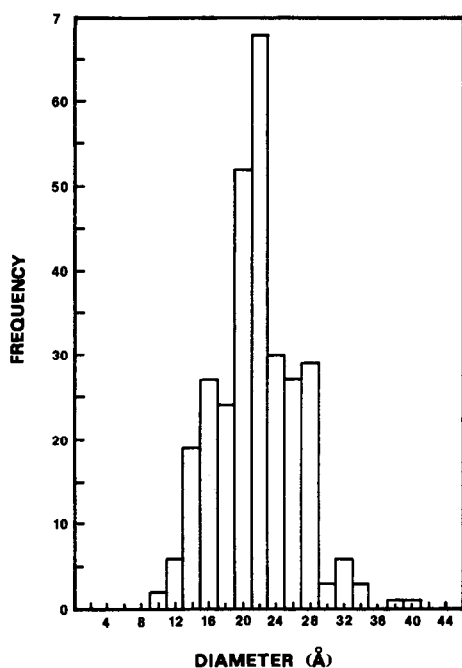


FIG. 8. Histogram of the particle diameters for the hydroxylamine hydrochloride preparation (4°C reaction temperature). The sample population was 300. The mean diameter is 22 Å, the median is 22 Å, and the standard deviation 5 Å.

followed by rapid reaction of the resulting ion. For both mechanisms the production of the reactive intermediate, i.e., BH_3 or $(\text{CH}_3)_2\text{HNBH}_2^+$, is first order with respect to H_3O^+ concentration.

It has been reported that, when DMAB is used in nickel electrodeless plating baths, varying amounts of Ni_2B are formed depending on the reaction conditions and concentrations (25). It is conceivable that platinum boride could be formed in reduction reactions involving DMAB (or possibly NaBH_4), but chemical analyses by Galbraith Laboratories have shown that the boron content of our samples is less than 0.05 wt%. Also, no platinum boride has been detected in our X-ray or electron diffraction studies.

1. 196-Å DMAB preparation. A successful procedure is to dilute 32 ml of 0.35 M

HCl and 40 ml of 1.0 g/liter PVP with glass-distilled water to a volume of 1984 ml at ambient temperature ($\text{pH} \approx 2$), and then to add 0.0352 g of DMAB while stirring the mixture rapidly. Three minutes after adding the DMAB, 16 ml of 0.015 M H_2PtCl_6 is injected into the solution. After another 3 min, the entire solution turns a dark golden brown. The time lapse between the first signs of darkening and the darkest solution is less than 5 sec. Approximately 20 min later the hydrosol is dialyzed, and then the hydrosol is dehydrated by freeze-drying in the conventional manner.

A typical electron micrograph of this preparation is shown in Fig. 9. Close examination of such micrographs reveals areas of light and dark contrast and in some cases Moiré fringes, which indicates that two crystalline domains with different crystallographic orientations are on top of one another. The Moiré fringes extended at most about 50 Å and several such sets of fringes could be observed at random orientations relative to each other within a single particle. Using the X-ray line-broadening method (26), the crystallite size for this preparation was found to be 46 ± 14 Å. However, it is unlikely that these microcrystals are the product of individual microcrystals growing together, because no individual small microcrystals are observed in the electron micrographs. These observations lead us to conclude that the microcrystals produced by DMAB reduction are not single crystals, but rather mosaic composites. A histogram of the platinum-particle diameter for the 196-Å DMAB preparation is displayed in Fig. 10.

In an attempt to elucidate how these microcrystals are formed, all reactant concentrations in this preparation were reduced by factors of 4, 8, and 16. The reaction required longer to reach completion upon dilution, and the color change no longer occurred abruptly after 3 min, but rather took place gradually. The change in color oc-

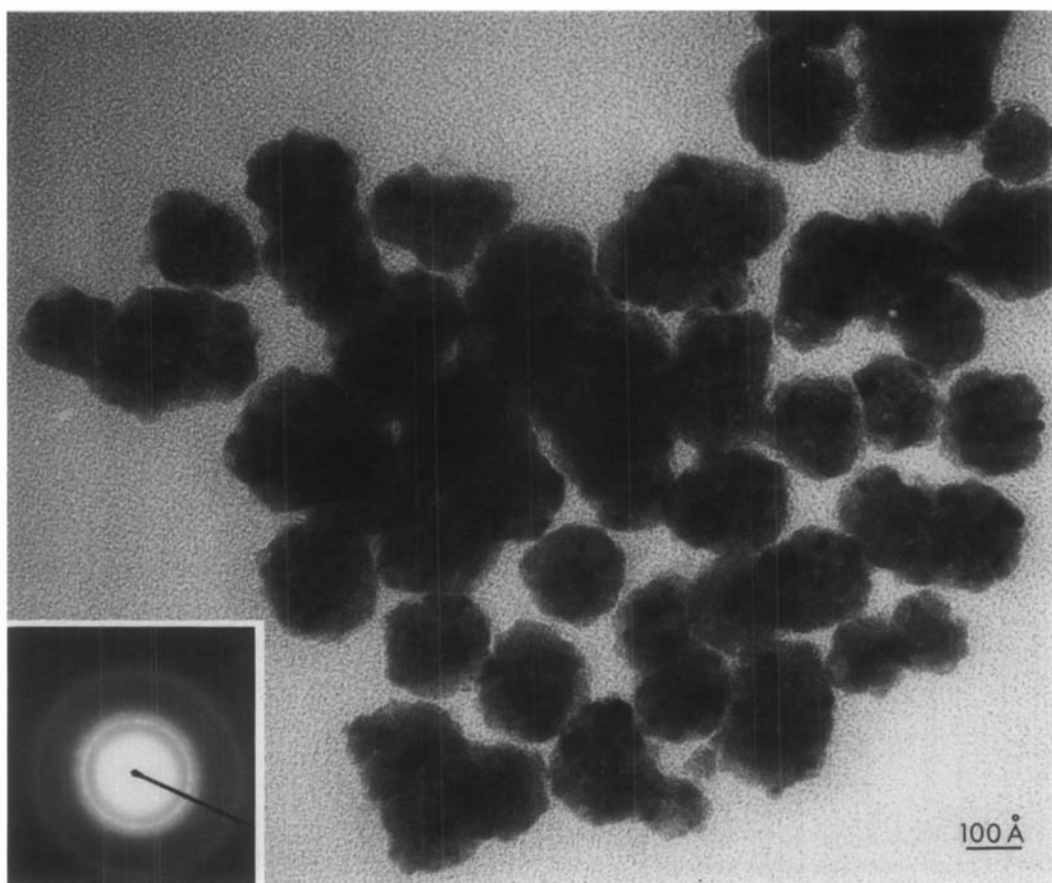


FIG. 9. Electron micrograph of a 196-Å DMAB preparation. An electron diffraction pattern for the preparation is shown in the lower left corner.

curred within a time interval of 6 to 7 min, 7 to 10 min, and 15 to 18 min for the 4-, 8-, and 16-fold dilution preparations, respectively. In each dilution experiment the electron micrographs showed about 30-Å-diameter microcrystals in sintered and unsintered states, but no smooth transition from composites to 30-Å microcrystals is observed. It is possible that another growth process, unrelated to the 196-Å preparation, occurs in the dilute regime in which only smaller microcrystals are formed. Hence, we have not been able to determine whether the polycrystalline structure of the

196-Å microcrystals is due to complete agglomeration of smaller microcrystals or to growth on nuclei under nonideal conditions, as manifested by high grain-boundary concentrations.

2. 113-Å preparation. This preparation is identical to the 196-Å preparation, except that no HCl is added ($\text{pH} \approx 7$). However, the color change occurs faster than for the 196-Å preparation, being on the order of 2 min, but the exact period is not as reproducible as it is in the latter preparation. As found in the 196-Å preparation, the electron micrographs again revealed mosaic com-

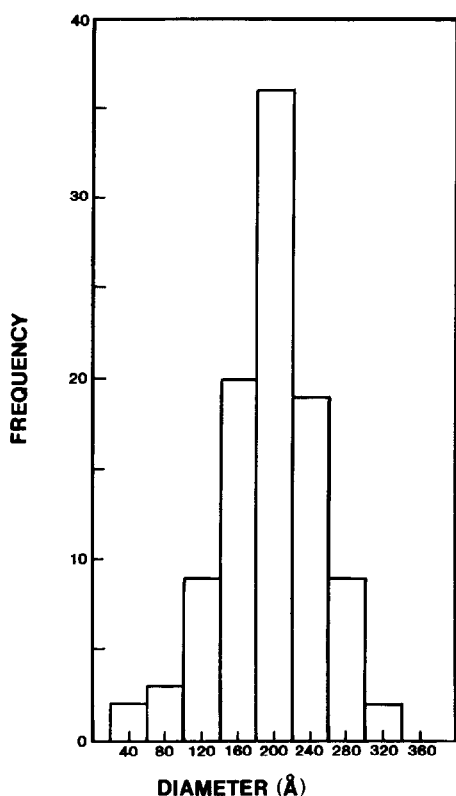


FIG. 10. Particle-size distribution for the 196-Å DMAB preparation. The sample population was 100. The mean diameter is 196 Å, the median is 199 Å, and the standard deviation is 55 Å.

posites and the absence of individual microcrystals. The particle size distribution for this preparation is depicted in Fig. 11.

3. Effect of pH. We have found that when the pH is 2, 196-Å microcrystals are formed and the induction period is almost 3 min. At a pH of 7, 113-Å microcrystals are produced and the induction period drops to 2 min. If the pH is increased from 7 to 10, the size of the microcrystals is unchanged, but the induction period is further reduced to 5–10 sec. Reduction will not occur if the pH is raised to 12.

Although a thorough kinetic study is necessary to completely explain these observations, some qualitative conclusions can be

drawn from the above data. Apparently the reduction of H_2PtCl_6 by DMAB depends on the concentration of a reaction intermediate whose formation is very pH dependent. Since the color change occurs suddenly after a definite induction period, the microcrystal formation must certainly be autocatalytic. Again, it is useful to examine the analogy to electrodeless plating, where a certain critical coverage of catalyst is necessary before deposition occurs. In microcrystal production, it is likely that a certain critical concentration of nuclei builds up during the induction period, followed by reduction of the remaining H_2PtCl_6 on these catalytic sites. The necessary critical concentration of nuclei may well depend on pH. Since larger microcrystals are formed at a pH of 2 rather than 7, possibly the criti-

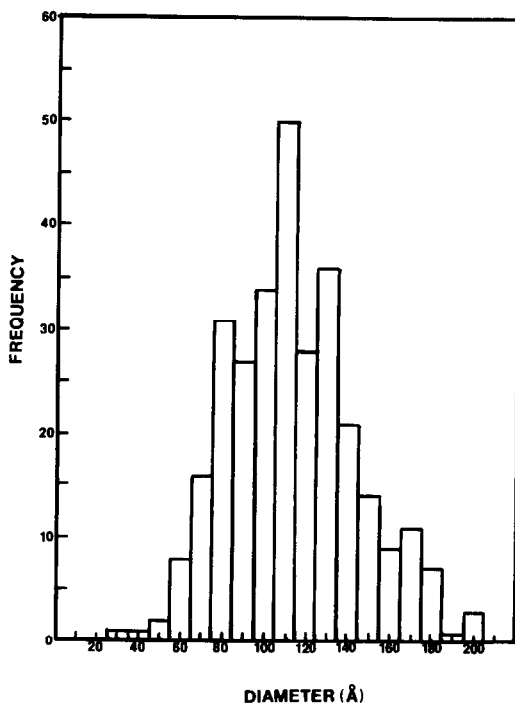


FIG. 11. Histogram of the particle diameters for the 113-Å DMAB preparation. The sample population was 300. The mean diameter is 113 Å, the median is 112 Å, and the standard deviation is 31 Å.

cal concentration of nuclei is less at lower pH. However, the induction period is longer at low pH, which contradicts the above hypothesis if the rate of formation of nuclei is independent of pH. However, reaction (10) becomes more important at lower pH, which retards the formation of nuclei and results in a longer induction period.

IV. Sodium Citrate Preparation

Very uniform microcrystals of platinum and gold can be produced using sodium citrate as the reducing agent (2, 27). The problem with this method is that a by-product of the reduction reaction acts as a protective agent for the hydrosol. We have verified this by observing that the hydrosol is stable without any additional protective agent. Also, chemical analysis by Galbraith Laboratories (Knoxville, TN) shows that the microcrystals contain about 3 wt% carbon, which is probably located at the surface of the microcrystals. Since we have been unsuccessful in isolating this by-product, further measurements of the physical and chemical properties of these microcrystals have been postponed until this is possible.

V. Other Reducing Agents

Several other reducing agents were tried in an attempt to synthesize microcrystals having different sizes. In particular, formaldehyde, hydroquinone, pyrocatechol, and 2,4-diaminophenol were incapable of reducing chloroplatinic acid, even at elevated temperatures. Sodium formate, hydrazine monohydrate, trimethylamine borane, and sodium trimethoxyborohydride were effective in reducing chloroplatinic acid, but problems were encountered with each of these reducing agents. Sodium formate produced clumped particles and only a partially stable hydrosol. Hydrazine monohydrate reduced chloroplatinic acid at high temperatures (80°C), but instantaneous precipitation occurred, even in the presence of

protective agents. Precipitation also occurred when trimethylamine borane was used, and sodium trimethoxyborohydride was unstable under the necessary reaction conditions. We feel that extensive work with the last two reducing agents could lead to successful preparations, in part due to their chemical similarity to DMAB and NaBH₄, respectively, where successful procedures have been developed. In the case of hydrogen peroxide, electron-diffraction studies of the resulting particles showed diffraction rings which were not characteristic of platinum.

VI. Protective Agents

Protective agents are usually necessary to avoid particle sintering, and several different ones were investigated during the course of this research. Historically, gelatin is the best known protective agent and has the lowest protective ratio. Protective agents with low protective ratios are desirable, because the microcrystals can contain a higher wt% platinum. Unfortunately, gelatin is made up of a complex mixture of proteins and is not as pure as many available synthetic polymers, so that it was not used extensively in our preparations.

Three promising synthetic polymers were examined: sodium polyacrylate (28), polyvinyl alcohol (5), and PVP (29). PVP turned out to be the optimum choice, both in terms of its very low protective ratio (≈ 0.13), i.e., the ratio of the mass of the protective agent to the mass of the microcrystals protected, and its high purity. PVP is an acetylase derivative and has the for-

mula $\left[\begin{array}{c} \square \\ | \\ \text{N} \\ | \\ \text{—CH—CH}_2\text{—} \end{array} \right]_n$. It is best to use an excess of PVP over the minimum protective ratio to ensure adequate protection. The only negative feature of PVP, like most protective agents, is that it is hygroscopic

TABLE I
WEIGHT-PERCENT PVP IN A TYPICAL 113-Å
DMAB PREPARATION

Element	Galbraith analysis	Gravimetric analysis
C	15.2 ± 0.3	
H	2.1 ± 0.2	
N	3.0 ± 0.2	
O	3.45 ± 0.2 ^a	
B	0.047 ± 0.005	
wt% PVP	23.8 ± 0.9	24.78 ± 0.02

^a Calculated from the molecular formula for PVP assuming 3 wt% N.

due to its tendency to hydrogen bond to water.

VII. Chemical Analyses

1. *Weight fraction of platinum.* The weight fraction of platinum in the platinum-microcrystal samples was analyzed gravimetrically in our laboratories and spectroscopically by Galbraith Laboratories. Since PVP is hygroscopic, all samples were stored under vacuum prior to being weighed to minimize exposure to water vapor. Aqua-regia-etched platinum foil (99.99% Pt) served as the sample container, and the empty container was weighed, filled with sample (≈ 25 mg), and then reweighed on a Cahn Model RG 2000 electrobalance to ± 1 μ g. All samples were heated in air to 800°C for 8 hr and then cooled in a dessicator and reweighed. The loss in weight was attributed to the removal of PVP from the sample, and independent sample analyses by Galbraith Laboratories was performed to confirm the validity of this technique. The analytical results for a typical 113-Å DMAB preparation are compared in Table I, and it is apparent that the results are in good agreement. The wt% PVP for our most successful preparations are given in Table II. For samples protected with PVP, the average wt% PVP is only 45.5% due to its low

protective ratio, so that platinum is a major constituent of these microcrystals.

2. *Chloroplatinic-acid analysis.* Since chloroplatinic acid is deliquescent, accurate solution concentrations cannot be prepared by simply weighing the solid reagent. It is also of interest to determine what percentage of chloroplatinic acid remains unreacted after reduction. For these reasons, a spectrophotometric technique based on Sandell's colorimetric method (30) was developed for use in the concentration range of interest ($\approx 5 \times 10^{-4}$ M). A Baush and Lomb Spectronic 20 spectrometer was employed for these measurements.

A standard platinum solution was made by dissolving 0.1000 g of 99.95% platinum wire in aqua regia, and this solution was evaporated to dryness and 5 ml of concentrated HCl and 0.1 g of NaCl were added. The resulting solution was again evaporated to dryness, and the residue was dissolved in 20 ml of a solution containing one part concentrated HCl and one part H₂O followed by dilution to 1 liter. The other necessary stock solution is a 10% solution of SnCl₂·2H₂O in 2N HCl. This solution is sensitive to oxygen and has a limited shelf life.

The following procedure was used to calibrate the spectrometer in terms of platinum concentration. An aliquote of the plati-

TABLE II
WEIGHT-PERCENT PVP IN
DIFFERENT
PLATINUM-MICROCRYSTAL
PREPARATIONS

Preparation	wt% PVP
Standard NaBH ₄	50.60
Reverse NaBH ₄	66.06
Strand NaBH ₄	0.00
4°C NH ₂ OH·HCl	59.30
113-Å DMAB	24.78
196-Å DMAB	26.86

num-containing solution was transferred to a 50-ml volumetric flask, and then 1 ml of concentration HCl and 9 ml of H₂O were added, followed by enough H₂O to make the volume 30 to 40 ml. Next, 2.0 ml of the stannous chloride solution was added and the resulting solution diluted with water to bring the solution volume to 50 ml. The solution was mixed and, after waiting 5 min, the present transmission was determined at 500 nm relative to a blank having all reagents except the platinum-containing solution. With this method, it is important that the HCl concentration of the 50 ml solution be about 0.3 M, which can be attained by either adding HCl or NaOH. A calibration curve was determined using 1-, 2-, 3-, 5-, and 10-ml aliquotes of standard platinum-containing solution. The following expression for the dependence of platinum concentration C_{Pt} on transmission T was derived from a computer fit of the data:

$$C_{Pt}(\times 10^{-4} M) = -0.0072 + 1.5534 \ln 1/T - 1.5485(\ln 1/T)^2 + 1.0896(\ln 1/T)^3. \quad (13)$$

The correlation coefficient squared for the curve fit was 99.9%, which attests to the excellent agreement between the above expression and the data.

Equation (13) was used to determine the chloroplatinic acid concentrations both before and after reduction. In the latter case, a known volume of freshly reduced hydrosol was placed in dialysis tubing and left to equilibrate in a bath of glass-distilled water of equal volume. The solution for spectrophotometric analysis was taken from this bath, and the concentration of unreacted H₂PtCl₆ was determined by correcting for the dilution factor. This procedure was used to eliminate microcrystals from the solution to be analyzed, since their presence would cause excessive light scattering. The mole percent of unreacted H₂PtCl₆ for several different preparations is given in Table III.

TABLE III
MOLE PERCENT UNREACTED H₂PtCl₆ in
Different Platinum-Microcrystal
Preparations

Preparation	mol% H ₂ PtCl ₆
Standard NaBH ₄	34 ± 5
Reverse NaBH ₄	50 ± 5
4°C NH ₂ OH·HCl	22 ± 5
113-Å DMAB	0 ± 1
196-Å DMAB	0 ± 1
Sodium citrate	26 ± 5

As discussed previously, competing reactions, such as reactions (3) and (7), lead to the incomplete reduction of H₂PtCl₆.

VIII. Particle-Size Distribution

Here we explore the possibility of describing the distribution of particle diameters for the spherical particles produced in our standard NaBH₄, reverse NaBH₄, 4°C NH₂OH·HCl, and sodium citrate preparations with a mathematical function, which will facilitate the determination of size-dependent properties. This function should predict a zero probability for finding microcrystals smaller than one platinum atom (diam ≈ 3 Å). Since all the particle-size distributions are skewed toward larger diameters, the Gaussian distribution is inadequate. Also, preparations having larger standard deviations, such as the NaBH₄ preparations, result in a finite probability of finding particles of zero diameter when a Gaussian function is used. Instead, we have found that the skewed distribution of particle diameters is characteristic of a log-normal distribution (17).

A log-normal distribution of particle diameters is simply a normal distribution of the logarithm of the particle diameters, $\ln d$, where $0 < d < \infty$. This distribution is skewed toward larger particle diameters and gives a very small probability of finding very small particles, as required by experi-

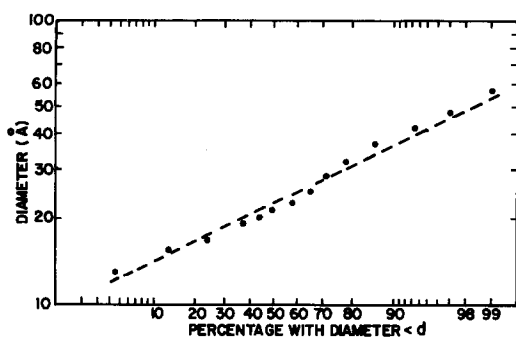


FIG. 12. Log-probability plot of the platinum-particle diameters from the reverse NaBH_4 preparation.

ment. A graphical test of the validity of the log-normal distribution is provided by plotting on logarithmic, probability paper, d versus the percentage of particles having a diameter less than d , which should result in a straight line if the log-normal distribution is obeyed. A typical log-probability plot is shown in Fig. 12, where it is apparent that the overall fit is reasonable. Likewise, the calculated mean and standard deviation from the log-normal distribution is in good agreement with those determined from the empirical particle-size distributions. At present we have no electron microscopic evidence for particles less than 10 Å in diameter, although it is difficult to identify such particles. Therefore, the particle-size distribution for these very small particles is uncertain, but based on the distribution of larger-particle diameters the log-normal distribution is probably appropriate.

Conclusions

In this study we have shown that it is possible to synthesize small platinum particles in the form of *spheres*, *strands*, and *composites* by the chemical reduction of H_2PtCl_6 . The morphology and size of the platinum particles depends on the nature of the reducing agent, the presence and type of protective agent, and the reaction condi-

tions. A summary of our findings for the most successful syntheses is given in Table IV.

Some of the advantages of this low-temperature synthetic method are that substantial amounts of sample can be prepared, the weight percentage of platinum is high, the equipment is inexpensive, and electron microscopy can be used to characterize the particles. This approach is chemically quite flexible in the sense that it can be extended to the synthesis of other types of elemental-metal particles, such as gold and palladium, by the chemical reduction of chloroauric and chloropalladic acids, respectively. It can also be modified to produce homogeneous alloy particles, such as platinum-gold and platinum-palladium alloys, by the chemical reduction of the corresponding mixed acids. Moreover, it is possible to attach either protected or unprotected particles to supports such as silica and alumina by immersing the support in the hydrosol. Finally, it has occurred to us that it should be possible to use this procedure to incorporate unprotected platinum or other metal alloy particles in the hydrosol state into biological systems, such as vesicles, to achieve high catalytic activity.

This work has set the stage for detailed investigations of the properties of these small platinum particles, which are currently being pursued in our laboratories. In

TABLE IV
SUMMARY OF RESULTS FOR THE SYNTHESIS OF SMALL PLATINUM PARTICLES BY THE CHEMICAL REDUCTION OF H_2PtCl_6

Preparation	Protective agent	Geometry	Diameter (Å)
Standard NaBH_4	PVP	Spherical	28 ± 11
Reverse NaBH_4	PVP	Spherical	25 ± 10
Strand NaBH_4	None	Strand	$\approx 60 \times n^a$
4°C $\text{NH}_4\text{OH}\cdot\text{HCl}$	PVP	Spherical	22 ± 5
113-Å DMAB	PVP	Composite	$\approx 113 \pm 31$
196-Å DMAB	PVP	Composite	$\approx 196 \pm 55$
Sodium citrate	None	Spherical	22 ± 4

^a n = strand length, $\geq 60\text{Å}$.

addition to the opportunity to elucidate their properties, it has come to our attention that the availability of these particles provides valuable particle-size standards for spectroscopic studies. (31).

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