

Size Characterization of Colloidal Platinum Nanoparticles by MALDI-TOF Mass Spectrometry

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Abstract

In this work, matrix assisted laser desorption ionization-time of flight (MALDI-TOF) mass spectrometry has been applied to characterize colloidal platinum nanoparticles synthesized in the 1 to 4 nm size range. These nanoparticles were prepared via a solution-based method in which the size could be tuned by varying reaction conditions, such as the alcohol used as a reductant. Poly(vinylpyrrolidone), or PVP, (MW = 29,000) was utilized as a capping agent to stabilize the synthesized particles in solution. A model for determining the size of the metallic nanoparticle core has been developed and verified through correlation with results from transmission electron microscopy (TEM) and x-ray diffraction (XRD) measurements. In addition, experiments performed with capped and uncapped nanoparticles indicate that one nanoparticle is capped by one PVP chain. These findings clearly indicate the usefulness of MALDI-TOF mass spectrometry as a technique for fully characterizing nanoscale materials, as well as to provide further insight into the role of the PVP capping agent during catalytic reactions in solution.

Keywords

Colloidal platinum; Nanoparticles; Poly(vinylpyrrolidone); Laser desorption/ionization mass spectrometry; Catalysis

Introduction

The application of nanoscale materials to areas such as drug delivery, sensing, hydrogen storage, and catalysis requires knowledge of a wide range of properties, the most important of which are size and structure. In catalysis, synthetic methods have been combined with characterization methods to develop a molecular-level picture of catalyst structure.¹ Nanoscale catalytic materials with well-controlled particle sizes and structures may be prepared using synthetic methods involving solution-based colloidal chemistry.²⁻⁴ These nanoparticles may be synthesized with finely-tuned sizes by a variety of reduction methods, and stabilized by different means to prevent aggregation in solution, with a common polymer stabilizer for platinum nanoparticles being poly(vinylpyrrolidone), or PVP. By tuning the particle size of a catalyst, selectivity may be controlled in a catalytic reaction.⁵ Achieving 100% selectivity in catalysis is important to eliminate waste from unwanted byproducts, thereby streamlining processes by removing separation steps.⁶ As a result, catalysis using these colloidal nanoparticles remains an active area of current research.

Colloidal Pt nanoparticles stabilized by PVP are catalytically active for a number of reactions, and in particular have been shown to catalyze several selective hydrogenations.⁷⁻¹³ In one instance, enhanced selectivity for the hydrogenation of 2-hexyne has been suggested to be the result of surface modification by the PVP capping agent.¹² In another case, the quantity of the PVP capping agent present has been observed to influence catalytic activity.¹³ Taken together, these findings suggest that for catalytic applications using these colloidal nanoparticles in solution, knowledge of both the interaction of the capping agent with the nanoparticle and the particle size are crucial for optimizing the activity and selectivity of catalytic reactions. With this information, tailored structures may be prepared, and since the amount capping agent present

is an important piece of information necessary for understanding factors that control the activity and selectivity of the catalytic reaction, characterization methods employed must analyze both the metallic nanoparticle core and the polymeric capping material.

Classical techniques for characterizing metal nanoparticle catalysts include transmission electron microscopy (TEM), powder x-ray diffraction (XRD), and physical adsorption. However, these methods cannot directly discern the amount or size of the capping agent. Matrix assisted laser desorption ionization-time of flight (MALDI-TOF) mass spectroscopy (MS) is a technique beginning to emerge as a useful tool for characterizing various types of nanomaterials.¹⁴⁻²⁷ MALDI-TOF mass spectrometry has an advantage over TEM and XRD in that it may be used to characterize extremely small nanomaterials, such as those with particle sizes less than 5 nm. Nonetheless, when coupled with either TEM or XRD for characterization of nanomaterials, MALDI-TOF MS may be used to determine the size and mass of the nanoparticle core, as well as the mass of the capping agent. As examples, in previous work, the sizes of gold nanoparticles¹⁴ and ZnS nanocrystals¹⁵ have been determined, and the calculated particle sizes agree well with the values found by TEM and XRD. These results clearly show the usefulness of MALDI-TOF MS in aiding to characterize a diverse selection of nanomaterials with various properties.

In this work, a MALDI-TOF mass spectrometry analysis of colloidal platinum nanoparticles, synthesized in the 1 to 4 nm size range using alcohol reduction methods, is described. Experiments performed with both PVP-capped and uncapped nanoparticles clearly indicate that individual nanoparticles are surrounded by a single polymer chain. Particle sizes were determined based on a model developed assuming one polymer chain per nanoparticle, as well as a spherical geometry for the metallic core. Comparison of particle sizes calculated based

on mass spectrometry data with those obtained using TEM and XRD shows good agreement between the three techniques. These findings clearly suggest the utility of MALDI-TOF mass spectrometry in fully characterizing nanoparticles used in a wide range of applications, such as catalysis. They also provide a clearer picture of the role played by the capping agent during catalytic reactions in solution involving these colloidal platinum nanoparticles.

Experimental Section

Platinum nanoparticles in the 1 to 4 nm size range were synthesized using a polyol method described in detail in the literature.²⁸ Poly(vinylpyrrolidone) (MW = 29,000 g/mol) and hexachloroplatinic acid ($\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$) were obtained from Sigma-Aldrich and used without further purification. Nanoparticles of a selected size were obtained by using a specific alcohol (ethylene glycol, methanol, or ethanol) as a reducing agent and by varying certain other experimental conditions.

The synthesized nanoparticles were then characterized using TEM, XRD, and MALDI-TOF MS. TEM images were recorded using a Topcon EM002B microscope at the National Center for Electron Microscopy at the Lawrence Berkeley National Laboratory. XRD patterns were obtained using a Bruker D8 GADDS diffractometer in the Department of Chemistry at the University of California, Berkeley. MALDI-TOF MS was performed at Lebanon Valley College using a Bruker OmniFlex LT MALDI-TOF instrument. Matrix solutions were composed of 20 mg of α -cyano-4-hydroxycinnamic acid (CHCA) dissolved in a 1:4 v/v solution of acetonitrile and deionized water. The sample solution was composed of a 1:10 v/v mixture of platinum nanoparticle colloid to matrix solution. Drops of 1 μL of the sample solution were placed on a stainless steel target and allowed to dry before insertion into the vacuum system. Mass spectra

were recorded based on the average of 200 shots of a nitrogen laser (337 nm) and using an acceleration voltage of 20 kV.

Results and Discussion

Displayed in Figure 1 is a TEM image for PVP-capped platinum nanoparticles synthesized using ethylene glycol as the reductant. The average size of these nanoparticles has been determined to 1.85 nm. This particle size also agrees well with results from XRD measurements, where a size of 1.85 nm was calculated using the Debye-Scherrer equation. As indicated in the Experimental Section, other nanoparticle sizes have also been prepared by varying reaction conditions, such as the alcohol used as the reductant. TEM results indicate these nanoparticle sizes to be 2.60 nm, 2.96 nm, and 3.07 nm, while XRD measurements yield nanoparticle sizes of 2.47 nm, 2.70 nm, and 3.15 nm, respectively. All of the TEM and XRD sizes reported in this work agree well with those reported in the literature for platinum nanoparticles prepared using these colloidal-based synthetic methods.²⁸ Hereafter, these colloidal platinum nanoparticles will be referred to by sizes determined using TEM.

In addition to having the particle sizes determined with TEM and XRD, the synthesized nanoparticles have also been characterized using MALDI-TOF MS. Shown in Figure 2 is a mass spectrum for PVP-capped 1.85 nm platinum nanoparticles. The spectrum exhibits a single peak over the 10,000 to 400,000 amu range. To find the average mass of these nanoparticles, two Gaussian peaks, one for singly-charged nanoparticles and the other for doubly-charged nanoparticles, were first fit to the mass spectrum using the software program Igor Pro. The average mass of the nanoparticles was then calculated to be 73,000 amu using an average value integral for the singly-charged nanoparticle peak. This calculated mass is higher than that

predicted from calculations done based on the TEM or XRD particle sizes. If one assumes that the nanoparticles are spherical ($V = \frac{4}{3} \pi r^3$), and that the nanoparticles have the same density ($\rho = \frac{m}{V}$) as that of bulk platinum ($\rho = 21.4 \text{ g/cm}^3$), one would calculate a mass of 39,000 amu using the relationship:

$$m = \rho \times \frac{\pi}{6} \times N_A \times d^3 \times 10^{-21} \quad (1)$$

where N_A is Avogadro's number, necessary to convert g to amu since $1 \text{ amu} = 1 \text{ g/mol}$, and d is the particle size in units of nm. The last factor converts nm^3 to cm^3 in order to cancel the remaining units. To understand the difference in these masses, MALDI-TOF mass spectra were also acquired of uncapped 1.85 nm platinum nanoparticles.

Presented in Figure 3 is the MALDI-TOF mass spectrum for uncapped 1.85 nm platinum nanoparticles. During the synthesis of this size nanoparticle, PVP is not added at the start of the reaction to control the size and to stabilize the nanoparticles. Instead, the nanoparticles are stabilized by a glycol-derived species, and are precipitated out of solution by the addition of strong acid.²⁹ The precipitated nanoparticles are then redispersed in a PVP-ethanol solution in order to be capped. For the data seen in Figure 3, unprecipitated nanoparticles were used directly for the preparation of the MALDI sample. As observed in the figure, the average mass of these uncapped nanoparticles was determined to be 42,000 amu. The difference between this mass and that of the capped nanoparticles is 31,000 amu, which is close to the mass of PVP. This finding clearly suggests that each nanoparticle is capped by one PVP chain. In order to verify that this result extends to nanoparticles of other sizes, MALDI-TOF mass spectra were recorded for the other synthesized nanoparticles.

PVP-capped platinum nanoparticles of 2.60 nm, 2.96 nm, and 3.07 nm in size were also analyzed using MALDI-TOF MS, and those spectra are found in Figure 4. As seen in the figure, the particle mass increases with an increase in the size of the nanoparticle. To calculate nanoparticle size using MALDI-TOF MS data, the mass of one PVP chain determined experimentally, 31,000 amu, was subtracted from the average nanoparticle mass, and the nanoparticle size was calculated in a manner similar to that described above for the 1.85 nm nanoparticles. All of the spectra contain peaks for both singly-charged and doubly-charged nanoparticles. The nanoparticle sizes calculated from the MALDI-TOF experiments are listed in Table 1, along with sizes from the TEM and XRD measurements. All three techniques display good agreement between each other. In addition, the MALDI-TOF average mass has been plotted versus TEM particle size, and this graph is shown in Figure 5. The data were fit using a third-order polynomial of the form

$$y = y_0 + Ax^3 \quad (2)$$

where y is the nanoparticle average mass, m_{avg} , in units of amu and x is the nanoparticle size from TEM in nm. As seen in the figure, the fit of the data points yields good results. The constant y_0 was set equal to 31,000 amu, which gave a value for the constant A of 6920 amu/nm³, a number close to that expected based on equation 1 (6750 amu/nm³). This observation provides evidence that the assumption of spherical geometry for these nanoparticles is reasonably correct, as well as confirms the finding that one nanoparticle is capped by one PVP chain. Taken together, the results of this work provide new insight into the application of these colloidal platinum nanoparticles in fields such as catalysis.

In light of the findings presented in this work, a clearer picture of the role played by the PVP capping agent during the course of a catalytic reaction in solution begins to emerge. This

polymer chain coils itself around the platinum nanoparticle, and the sidegroups interact with the nanoparticle surface. It is currently believed that charge transfer occurs between the carbonyl functional group in the pyrrolidone ring and the platinum nanoparticle surface.³⁰⁻³¹ This type of bonding would lead to a strong interaction that traps the particle in the inner region of the coiled polymer, thus creating a hydrophobic environment around the nanoparticle that would be beneficial for certain types of catalytic reactions, such as hydrogenations. In fact, a recent study has pointed to PVP-Ru nanocatalysts displaying this behavior for C=O and C=C hydrogenations.³² As the polymer molecular weight is increased, the size of this hydrophobic environment would increase, thereby leading to the observed increase in catalytic activity. Due to the hydrophilic nature of PVP, which renders it soluble in water, and the ability to create this hydrophobic region around the metal nanocatalyst, these PVP-capped nanoparticles may be utilized in “greener” catalytic reactions that currently require organic solvents. Additionally, as mentioned previously, the groups bonded to the nanoparticle surface could also serve as site modifiers that could increase the selectivity of certain reactions.¹² With the ability to control the size and shape of the nanoparticle core, as well as the size of the PVP capping agent, highly active and selective catalysts may be tailored specific to each reaction.

Conclusion

In summary, it has been demonstrated that MALDI-TOF MS may be applied to characterize the size of PVP-capped platinum nanoparticles, which in turn leads to a better understanding of the molecular-level behavior of these materials as catalysts. Particle sizes determined from mass spectra were found to be in good agreement with those found by TEM and XRD measurements. In addition, it was also observed in the experimental findings that one PVP

chain caps one platinum nanoparticle. These methods could easily be extended to colloidal metal nanoparticles with other metals such as Rh, Pd, or Ru, and with other capping agents, such as dendrimers. This general applicability makes MALDI-TOF MS useful for characterizing a wide range of nanomaterials, thereby providing key information on structure-reactivity relationships important in fields such as catalysis.

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Table 1. Particle masses calculated from MALDI-TOF mass spectra and particle sizes, d, calculated from MALDI-TOF MS, TEM, and XRD measurements.

total mass (amu)	Pt core mass (amu)	d, MALDI (nm)	d, TEM (nm)	d, XRD (nm)
73,000	42,000	1.84	1.85	1.85
140,000	109,000	2.52	2.60	2.47
187,000	156,000	2.84	2.96	2.70
260,000	229,000	3.23	3.07	3.15

Figure Captions

Figure 1. TEM image of PVP-capped platinum nanoparticles synthesized by reduction in the presence of ethylene glycol.

Figure 2. MALDI-TOF mass spectrum of 1.85 nm PVP-capped platinum nanoparticles.

Figure 3. MALDI-TOF mass spectrum of 1.85 nm uncapped platinum nanoparticles.

Figure 4. MALDI-TOF mass spectra of selected sizes of PVP-capped platinum nanoparticles.

Figure 5. Plot of nanoparticle mass as a function of size determined by TEM.

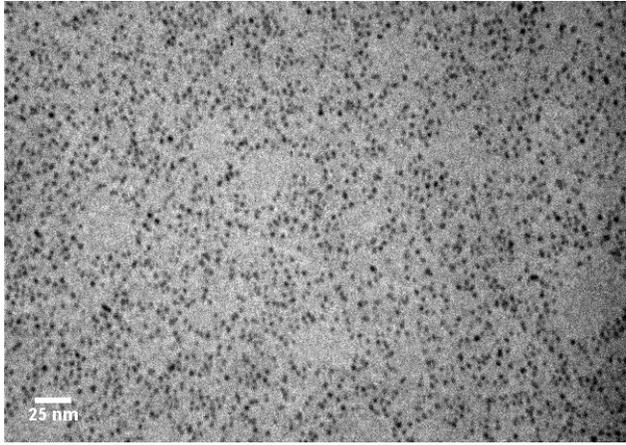


Figure 1

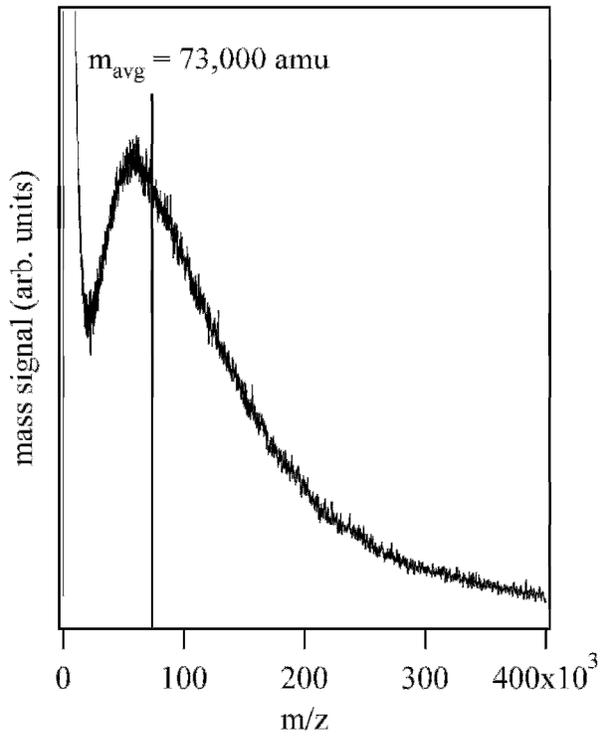


Figure 2

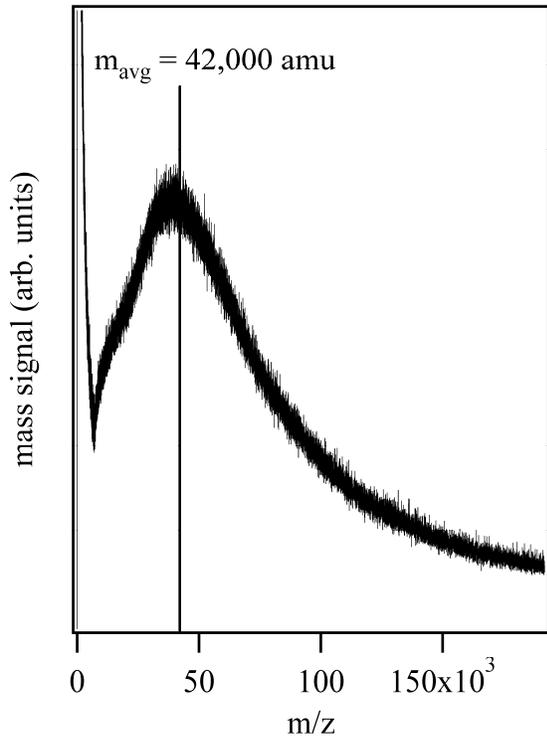


Figure 3

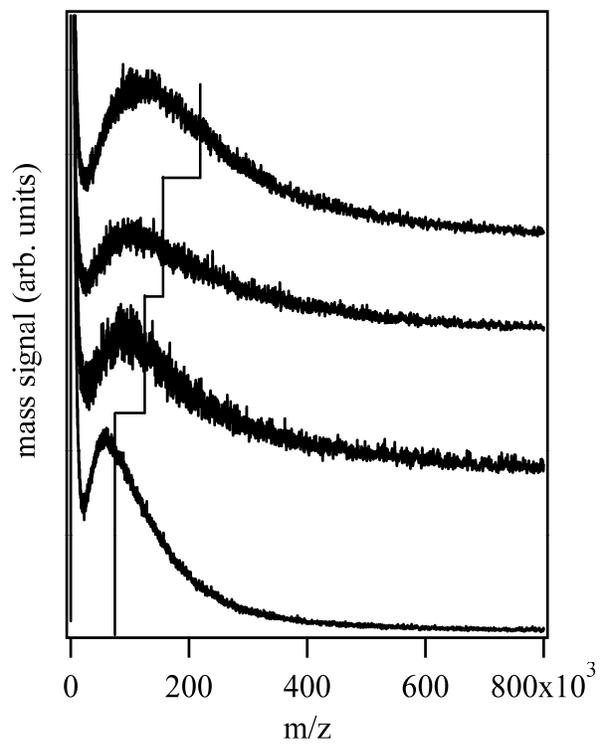


Figure 4

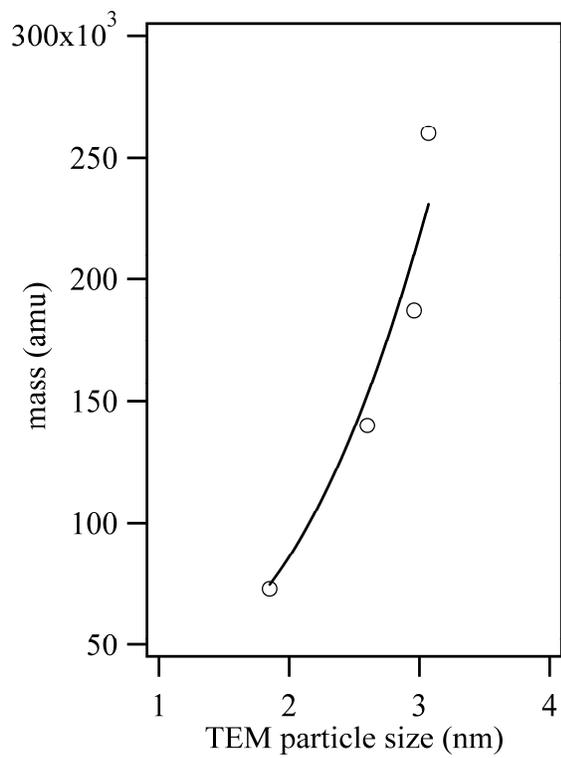


Figure 5

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