

## The Preparation of Platinum Nanoparticles on Titanium Using Chemical Reductive Growth Procedures

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**Abstract.** The synthesis of platinum nanoparticles by reduction of  $\text{H}_2\text{PtCl}_6$  with ascorbic acid has been studied. By high-resolution electron microscope and XRD analyses, the resultant nanoparticles have been found to be pure platinum of fcc structure. Their sizes were observed to increase with the increases chemical reductive with 24h. Then, platinum nanoparticles directly attached to Ti plates (Pt nanoparticles/Ti) were successfully fabricated. In this method, platinum nanoparticles could be grown on the Ti surface via the one-step immersion into the growth solution containing  $\text{PtCl}_6^{2-}$  and ascorbic acid. The attached and grown platinum nanoparticles were spherical having an agglomerated nanostructure composed of small nanoclusters. The present Pt nanoparticles/Ti may be promising for a new type of electrode material.

### Intorduction

A topic of rapidly burgeoning interest in nanoscience concerns the chemical, physical, and structural properties of metal nanoparticles, especially as a function of particle size, prompted by a myriad of potential applications in catalysis, as chemical and biosensors, and in microelectronics[1,2]. Many of these applications will be facilitated by developing methods for attaching such nanoparticles to surfaces in recent years because the unique properties of metal nanoparticles, such as optical, electronic, magnetic, and catalytic properties, can be added onto the characteristics of the attached surfaces. Various attachment methods of metal nanoparticles are available nowadays, including physical and chemical methods, such as casting, metal evaporation, electrochemical deposition, chemical impregnation reduction, the use of bridging reagents, etc[3].

Although a suitable method has been adopted to attach metal nanoparticles depending on the research purposes and/or the characteristics of the substrate surfaces, the colloid-based nanoparticle synthesis combined with bridging reagents would be a better method with respect to the uniformity of the nanoparticles. nanoelectrode ensembles[4,5]. Although many papers have been devoted to the modification of Pt nanoparticles on carbon, platinum, and gold electrode substrates[6-8], reports of the attachment of Pt nanoparticles on Ti are very scarce in comparison with the works on Au or Ag nanoparticle-attached ITO.

In this paper, We are interested in the preparation and characterization of Pt nanoparticles and Pt nanoparticles films on Ti plate without using bridging reagents. By applying the seed-mediated growth approach, the one-step in situ chemical reduction of  $\text{PtCl}_4^{2-}$  by ascorbic acid, which was originally developed for the formation of Pt nanoparticles in solution, we succeeded in attaching the Pt nanoparticles a onTi surfaces.

### Experimental Section

$\text{K}_2\text{PtCl}_6$ ,  $\text{NH}_3$ ,  $\text{H}_2\text{O}_2$  and ascorbic acid were obtained from Aldrich. Ti plates were purchased from Johnson Matthey (purity > 99.99). In all the procedures and the preparation of solution, we used pure water prepared using Millipore Autopure WR600A (Millipore, Ltd., resistivity > 18 MΩ).

The particle sizes were determined by transmission electron microscopy (TEM) using a Hitachi Model HF-2000 Field Emission Transmission Electron Microscope. The sample for TEM analysis was obtained by placing a drop of the dispersed solution onto a Formvar-covered copper grid and

evaporating it in air at room temperature. Before withdrawing the samples, the dispersed solutions were sonicated for 1 min to obtain the better particle dispersion on the copper grid. For each sample, usually over more than 100 particles from different parts of the grid were used to estimate the mean diameter and size distribution of particles. The surface morphology of the Pt nanoparticles attached to the Ti surfaces was characterized with a field-emission scanning electron microscopy (FE-SEM, JSM-7400F, JEOL, Japan). X-ray diffraction (XRD) measurements were performed on a Rigaku D/max III.V X-ray diffractometer using  $\text{CuK}\alpha$  radiation ( $\lambda = 0.1542 \text{ nm}$ ). UV-vis absorption spectra were recorded using a Cary 500 Scan UV-vis-NIR spectrometer (Varian Co.)

Typical procedures to chemical reductive of Pt nanoparticles are as follows: First, 0.5 mL of 50 mM  $\text{K}_2\text{PtCl}_6$  solution was added into 20 mL of pure water. 1.0 mL of 0.50 M ascorbic acid was added into the solution and the solution was left for a constant time (6, 12, 18, and 24 h.) at room temperature.

Ti plates were mechanically polished with 1500 grade emery paper. After polishing, Ti substrates were cleaned by immersion in boiling ethanol for 10 min, rinsed with water, and dipped for 10 min in warm 7:3 (v/v)  $\text{NH}_3/\text{H}_2\text{O}_2$  aqueous solution. Substrates were then rinsed three times in pure water, 2 min each time, and dried in air or under a nitrogen flow. Then, a carefully cleaned piece of Ti was immersed into the  $\text{K}_2\text{PtCl}_6$  solution. After that, ascorbic acid solution was added into the solution containing the Ti piece. Then, the Pt nanoparticles that directly attached Ti plates were removed from the solution, and rinsed with pure water several times, then dried with nitrogen gas for the FE-SEM characterization. If the Ti plates was immersed after the addition of ascorbic acid or during the Pt nanoparticles formation process, the attachment of Pt nanoparticles was possible. However, the attached density became lower in such cases. Thus, we show the results prepared in the above conditions.

## Results and Discussion

During the chemical reductive growth process, the color of the solution gradually turned from pale yellowish-brown to darkish, confirming the formation of Pt colloids in the aqueous phase. Fig 1 shows the absorption spectra of the Pt nanoparticles samples fabricated with different immersing times (6, 12, 18, and 24 h) in the growth solution. The absorbance around 350 nm increased with an increase of the growth period, accompanying a slight red-shift of the absorption maximum. This implies that the growth of Pt nanoparticles proceeded with an increase in the reduction time. However, compared with the increase until 18 h, the absorption observed after 24 h of growth did not exhibit a significance increase. Thus, the growth processes may be saturated before 24 h.

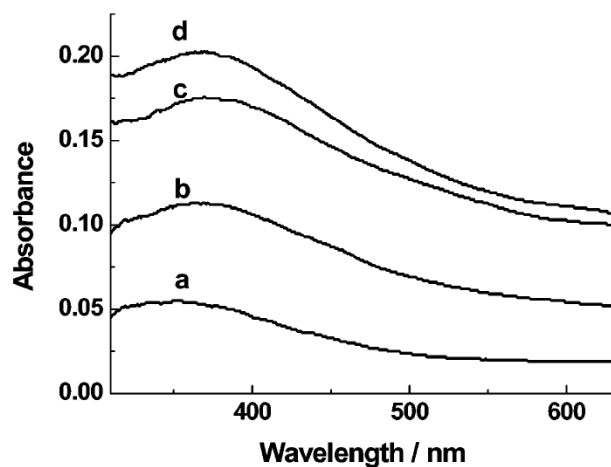


Fig 1. UV-visible absorbance spectra of the Pt nanoparticles solution fabricated with different growth times: (a) 6, (b) 12, (c) 18, and (d) 24 h.

In the formation process of the Pt colloid from  $\text{PtCl}_6^{2-}$ , it is known that the UV-vis absorption transforms from that with a peak of  $\text{PtCl}_6^{2-}$  at 258 nm to the featureless one, in which the absorption merely increases with the decrease of wavelength[9,10]. However, the absorption of Pt nanoparticles grown over several tens of nanometers is not well known. Thus, for recognizing the exact grown-up structures of Pt nanoparticles in solution, we observed the FE-SEM images of it.

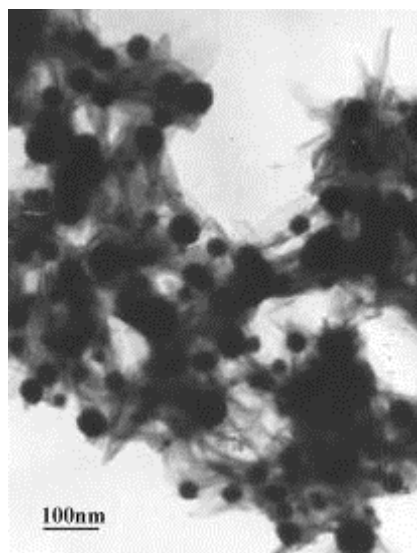


Fig 2 Typical TEM images of the Pt nanoparticles in solution

Fig 2 shows the typical TEM images of the surface of Pt nanoparticles that was prepared by mix the growth solution for 24 h. As shown in the Fig 2, it was found that the Pt nanoparticles, which were recognized as black dots with keeping a moderate dispersion. The shape of Pt nanoparticles was almost spherical, the diameters of the spherical Pt nanoparticles ranged from ca. 30 to 70 nm (see Fig 3). In this work, the size irregularly observed in Fig 2 also implies that the Pt nanoparticles proceeded via the progressive nucleation where the nucleation rate is low and nuclei are continuously formed during the chemical reductive processes.

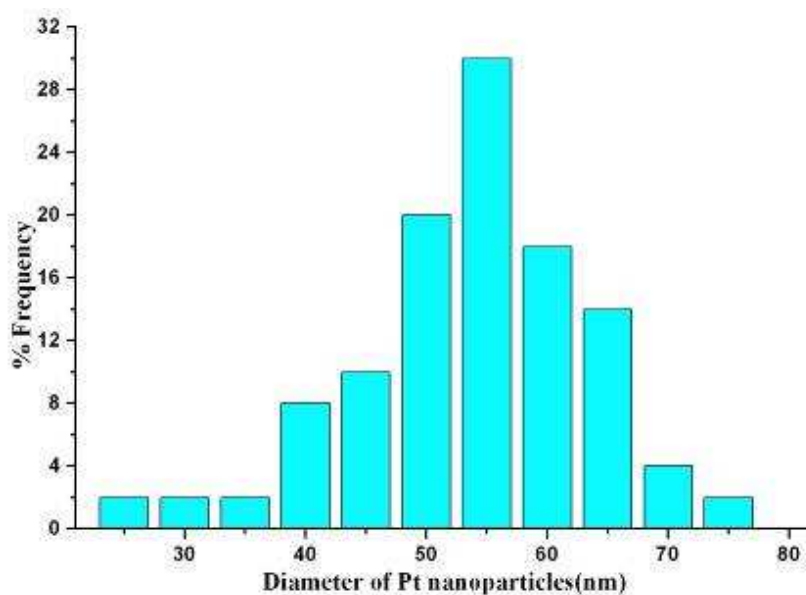


Fig 3 Histogram showing the diameter of Pt nanoparticles in solution

The X-ray diffraction of as-synthesized Pt nanoparticles in the typical synthesis are shown in Fig 4. Three characteristic peaks for platinum ( $2\theta = 40, 46.4,$  and  $67.6$ ), marked by their indices ((111), (200), and (220)), were observed. This revealed that the resultant particles were pure fcc platinum. it could be concluded that the ultrafine particles prepared in this work were pure platinum of fcc structure.

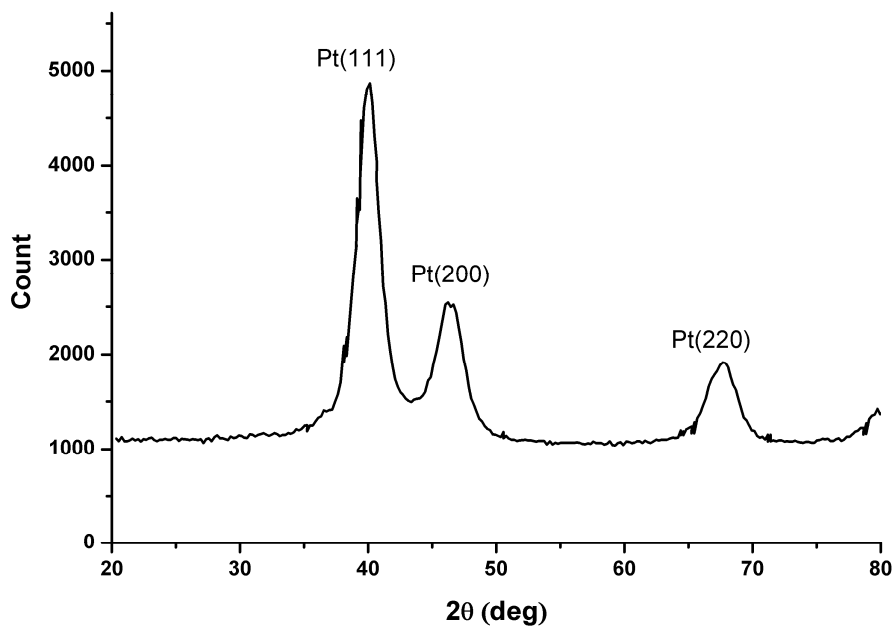


Fig 4 XRD patterns of Pt nanoparticles

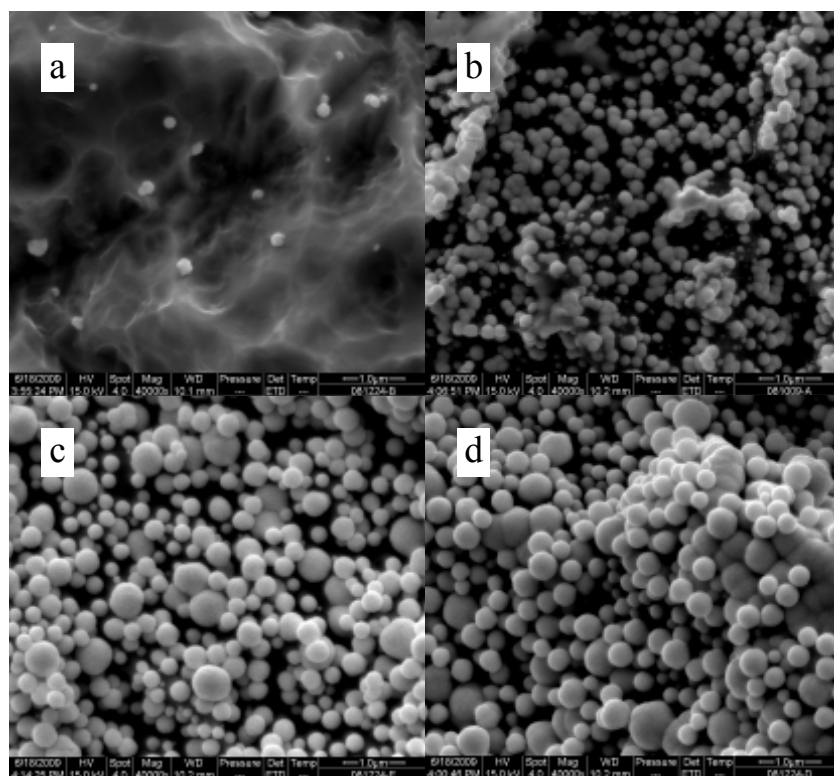


Fig 5. FE-SEM image of the Pt nanoparticles/Ti samples prepared with different reduction times; (a) 6, (b) 12, (c) 18 h, (d) 24h.

To elucidate the in situ chemical reductive growth in more detail, we observed the FE-SEM images of the Pt nanoparticles/Ti samples prepared with the different reduction times (6, 12, 18 and 24 h). Fig 5 shows the typical FE-SEM images. After 6 h of reduction (Fig 5A), Pt nanoparticles were observed to attach sparsely on the Ti plates surface. The sizes of the Pt nanoparticles were between 10 and 60 nm. After 4 h of reduction (Fig 5B), the density of Pt nanoparticles was apparently increased in comparison with that in Figure 5A, with the size distribution between 10 and 100 nm. The average diameter was increased after 18 h of reduction as shown in Fig 5C. However, the small Pt nanoparticles of ca. 10 nm could be observed on the surface also in this case. Compared figure 5C with fig 5D, the diameter of Pt nanoparticles observed after 24 h of growth did not exhibit a

significance increase. The present Pt nanoparticles exhibited the agglomerated nanostructures as if small nanoclusters were gathered to form the spherical structure in figure 5D. Thus, the morphological changes in the FE-SEM images with the reduction time also support the progressive nucleation mechanism. This result is in accord with above.

## Conclusions

Platinum nanoparticles have been synthesized in water solution by the reduction of platinum salt with ascorbic acid. The resultant particles have been characterized to be pure fcc platinum. The main controlling factors for the size of platinum nanoparticles size formed were chemical reductive time within 24h. With the increase of chemical reductive time, the size of platinum nanoparticles increased and then reached a constant when the time to 24h. In addition, we successfully fabricated the Pt nanoparticles/Ti by the in situ chemical reduction growth of Pt nanoparticles on the Ti plates surface. It was clarified that the amount of attached platinum nanoparticles could be tuned by changing the growth time, though it was difficult to obtain the monodispersed platinum nanoparticles due to the nature of this growth process.

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