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**SPUTTER DEPOSITION AND
FORMATION MECHANISM OF
PT AND PT ALLOY
NANOPARTICLES**



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1 General Introduction

Nanoparticles (NPs) are defined as particulate dispersions or solid particles with a size in the range of 10-1000nm.¹ Platinum (Pt) NPs have been intensively investigated because of their unique catalytic,² and also drawn attention as sensor³ or applied in biomedical field.⁴ However, the widespread commercialization and deployment of Pt catalyst is still limited by their high cost. For example, the cost of Pt in a hydrogen polymer electrolyte membrane fuel cell (PEMFC) for a 100 kW (134 hp) vehicle is much higher than that for an entire 100 kW gasoline engine. According to the cost reduction targets set by the U.S. Department of Energy (DOE), the total Pt catalyst loading (on both anode and cathode) in a membrane electrode assembly (MEA) must be reduced to below 0.125 mg·cm⁻².⁵ Meanwhile, in comparison to monometallic Pt NPs, Pt-based (Platinum/Copper (Pt/Cu),⁶⁻⁹ Platinum/Gold (Pt/Au),¹⁰⁻¹² etc.) alloy NPs are recently attracting much attention as they include smaller contents of Pt and exhibit higher catalytic activities.

The catalyst performance can be sensitive to metal particle size because the surface structure and electronic properties can change greatly in the 1–50 nm size range. It is also important for the nanoparticle catalyst to have a relatively narrow particle size distribution.¹³ Thus, a great effort has been devoted into how to synthesize particles with small size and narrow size distribution. Pt, Pt/Cu, and Pt/Au alloy nanoparticles have been prepared using radio frequency sputtering, reverse micelles, electron beam lithography and chemical vapor deposition techniques.

Among these methods, considerable research efforts have been devoted to prepare catalysts by chemical methods, for example, Pt NPs synthesized by chemical methods with stabilizers such as poly(vinyl pyrrolidone) (PVP),¹⁴ 3-(N,N-dimethyldodecylammonio) propanesulfonate (SB12),¹⁵ etc. Pt/Cu alloy NPs are obtained by chemical reduction routes⁶⁻⁸ using strong reducing agents⁷ or at high temperatures.^{6, 8-9} Pt/Au alloy NPs synthesized by chemical methods reported by other groups.¹⁶⁻¹⁹

However, NPs prepared by chemical reduction methods often use the reducing agents and contain byproducts which can influence the catalytic properties.²⁰ In order to synthesize small particles, stabilizer is needed, which is also reduce the catalytic activity if it is not removed completely. However, removal of these stabilizers requires harsh treatment such as thermal treatment^{15, 20} or acid treatment.²⁰ On the other hand, in the case of synthesis of alloy NPs, due to different reduction potential of metal ions, core-shell structure or phase segregation has been observed.²¹⁻²²

Recently, metal NPs synthesized by sputtering onto a liquid matrix have been reported.²³ NP synthesis by vacuum sputtering onto a liquid matrix is a green method because it neither uses toxic reducing agents nor produces any by-products.²⁴⁻²⁵ The method is very versatile in terms of controlling the size of the obtained NPs. In addition, choosing a liquid matrix with a good stabilizing ability can inhibit NP aggregation and help in controlling their growth. When a metal target is attacked by gaseous ions, metal atoms or clusters (aggregation of several atoms) are ejected; these collide with each other multiple times to form NPs.

1 Experimental Section

1.1 Preparation of Pt, Pt/Cu and Pt/Au alloy nanoparticles

Before using for sputtering, polyethylene glycol (PEG, average molecular weight 600, purchased from Junsei) was heated under vacuum condition at 80 °C for 2 h to remove water and dissolved gases. And then PEG (10 mL) was added in a petri dish with a diameter of 60 mm ϕ . The petri dish was placed in the sputtering chamber whereas the surface of the liquid was positioned 50 mm (single target sputtering) and 110 mm (double target sputtering) away from the metal target. After multiple times of Ar (99.99% purity) purging and evacuation, the pressure of the chamber was set at 2 Pa with Ar as carrying gas. A mechanical stirrer was used to stir the liquid at the stirring speed of 80 rpm. Sputtering was performed for 10 min to clean the target surface prior to collect NPs in PEG. Sputtering was performed with current varied from 5 to 50 mA on a collodion coated copper TEM grid and onto PEG. PEG temperature was set at 30 °C. Sputtering onto grid performed for 1 - 30 s. The sputtered NPs dispersed in PEG were stored at room temperature in dark for various periods of times (as synthesized to 5 months) to study the stability and particle growth after sputtering. Varying sputtering parameters to study the growth mechanism and formation mechanism.

1.2 Characterization

Size, size distribution and shape of the obtained NPs were analyzed by a JEOL

JEM-2010 and a JEOL-2000FX transmission electron microscopy (TEM) operating at 200 kV. TEM samples were prepared by dipping the collodion-coated Cu grid in PEG contain Pt NPs, followed by taking out the grid then gently dipping it in ethanol for 7 min to dissolve PEG. Finally, the grids were dried in the air for a few minutes at room temperature. The histograms of nanoparticle size distribution were obtained by measuring approximately 300 particles from at least 3 different regions of grid using ImageJ software. High resolution images of NPs were collected on a scanning transmission electron microscope (STEM, JEOL JEM-ARM200F, 200 kV). Optical absorption spectra in UV-Vis region were obtained using a JASCO V-630 spectrophotometer using a quartz cuvette with 1 mm optical path. Chemical state of Pt NPs was investigated by JEOL JPS-9200 X-ray photoelectron spectroscopy (XPS) device equipped with a monochromatic Mg K α source operating at 100 W under ultrahigh vacuum ($\sim 5.0 \times 10^{-7}$ Pa) conditions. Binding energies were referenced to the Si 2p binding energy of the Si wafer substrate. The crystalline structure of NPs was determined using X-ray diffraction (XRD, Rigaku Mini Flex II, Cu K α). C powder and methanol were added to PEG dispersion of Pt NPs. Pt, Pt/Cu and Pt/Au on C powder was collected by centrifugation and washed several times with methanol, then dried for XPS and XRD measurement.

2 Results and discussion

Synthesis of highly uniform Pt NPs with small size (below 2.0 nm) and narrow size distribution by sputtering of Pt onto polyethylene glycol (Mw. = 600) is the topic of chapter 2. The results indicate that particle sizes were tailorable from 0.9 ± 0.3 nm to 1.4 ± 0.3 nm by varying the sputtering current (5 – 50 mA) with negligible particle aggregation occurred in PEG during sputtering. It is found that a slight growth of particle size after sputtering can be attributed to the addition of free Pt atoms to the existing Pt NPs. All samples formed stable dispersions in PEG for 5 months storage. This result suggests an advantage of using a liquid matrix to produce and stabilize NPs.

Chapter 3 in the thesis is devoted for the synthesis of well-dispersed and stable Pt/Cu alloy NPs and studying growth mechanism of the alloy NPs in sputtering of Pt/Cu alloy target onto PEG. The effects of sputtering current, rotation speed of the stirrer, sputtering time, sputtering period, and temperature of PEG on the particle size are studied systematically. The key results demonstrate that the aggregation and growth of Pt/Cu alloy NPs occurred at the surface as well as inside the liquid polymer after the particles landed on the liquid surface. According to particle size analysis, a low sputtering current, high rotation speed for the stirrer, short sputtering period, and short sputtering time are found to be favorable for producing small-sized single crystalline alloy NPs. On the other hand, varying the temperature of the liquid PEG does not have any significant impact on the particle size. Thus, these findings shed

light on controlling NP growth using the newly developed green sputtering deposition technique.

Chapter 4 targets to the synthesis and formation mechanism of Pt/Au alloy NPs in a wide composition range by simultaneous sputter deposition of two independent magnetron sources onto PEG (Mw. = 600). The resulting NPs are alloy with the face-centered cubic (fcc) structure. It is observed that the particle sizes, composition, and shape are strongly correlated. On the other hand, these characteristics can be tailored by varying sputtering parameters appropriately. Large agglomerates are formed at Pt content less than 20 at. %, showing partial alloy structure. Highly dispersed NPs with no agglomeration in PEG can be obtained when Pt is more than 34 at. %. Moreover, a small amount of Pt could terminate the agglomeration of Au when sputtering on TEM grid. Experimental results for 30 min sputtering onto PEG for various sputtering currents, as well as computational simulations, indicate that using the formation energy and selective attachment during particle formation can be used for explaining the composition-dependent particle-size of Pt/Au NPs.

3 Conclusions

The results indicated that we can prepare highly uniform Pt NPs with size below 2.0 nm and narrow size distributions. Particle sizes were tailorable by varying the sputtering current (5-50 mA) whereas negligible particle aggregation occurred in PEG during sputtering. Our finding showed that after 10 days, Pt NPs were slightly

increased, of ca. 0.3~0.5 nm, in sizes due to the addition of free Pt atoms to the existing Pt NPs in PEG. Pt NPs were stable in PEG after 5 months with negligible particle aggregation, indicating the polymer matrix effectively stabilize NPs.

Stable Pt/Cu alloy NPs with diameters in the range of 1–3 nm and narrow size distribution were successfully synthesized at room temperature without using a reducing agent. Particle sizes could be tailored by varying the sputtering current, rotation speed of the stirrer, sputtering period, sputtering time, and PEG temperature. Compared with the samples sputtered onto TEM grids, particle growth could be inhibited to some extent using PEG as the capture medium without an additional stabilizing agent. It was found that decreasing the sputtering time, sputtering period, and sputtering current or increasing the rotation speed of the stirrer resulted in smaller Pt/Cu alloy NPs; there were no significant differences in the NP size with respect to the liquid matrix temperature (20–50 °C) over a sputtering period of 30 min. We proved that aggregation and growth of Pt/Cu alloy NPs occurred both on the PEG surface and inside the liquid bulk. Understanding the growth mechanism of NPs formed via sputtering onto liquid polymers allows good control over the size and shape of colloidal NPs and in achieving NPs with the desired properties. Our results indicate that the aggregation, growth, and colloidal stability of NPs during and after sputtering onto PEG are highly dependent on the metals used.

For the synthesizing Pt/Au alloy NPs, we have successfully demonstrated that the well-controlled Pt/Au alloy NPs with tuned composition was fabricated at room temperature by means of a co-sputtering method which is free of byproducts and

additives, despite the fact that the bulk metals exhibit a miscibility gap, and the formation mechanism were investigated for the first time. More importantly, the control of particle size, morphology, composition, and alloy formation were obtained by simply control of the sputtering parameter at the present experimental conditions. Our results show that the composition of Pt and Au can be modulated from ca. 20 to 100 atom % Pt in individual Pt/Au alloy NPs. In addition, the shape of the NPs generated at high Pt content (Pt at.%>27%) is spherical, the shape anisotropy increases with an increase of the Au content. A decrease in the particle size with increasing Pt content is observed and particles with same composition had similar sizes. The STEM-EDS results show that compared with nominal composition, there are more Pt existing in the edge of the nanoparticle and more Au existing in the center of the nanoparticle. Size, shape, and agglomeration degree of Pt/Au NPs are key points for their applications. Our findings in the relation among particle size, particle composition, and agglomeration state of the formed NPs with respect to their composition can shed light into the formation mechanism of Au-based and Pt-based alloy NPs. The atomic-level alloy of Pt/Au NPs with variable and controllable sizes are expected to be useful as effective catalysts for various reactions. A study of the catalytic performance of Pt/Au alloy NPs is currently in progress. These findings have profound implications to the design of Pt/Au alloy NPs in liquid and provide information for Pt-based and Au-based alloy synthesis, more intensive studies are currently underway.

4 References

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