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Ultra-small platinum and gold nanoparticles by arc plasma deposition

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ABSTRACT

Ultra-small (<2 nm) nanoparticles of platinum and gold were produced by arc plasma deposition (APD) in a systematic way and the deposition behavior was studied. Nanoparticles were deposited on two dimensional amorphous carbon and amorphous titania thin films and characterized by transmission electron microscopy (TEM). Deposition behavior of nanoparticles by APD was studied with discharge voltage (*V*), discharge condenser capacitance (*C*), and the number of plasma pulse shots (*n*) as controllable parameters. The average size of intrinsic nanoparticles generated by APD process was as small as 0.9 nm and deposited nanoparticles began to have crystal structures from the particle size of about 2 nm. *V* was the most sensitive parameter to control the size and coverage of generated nanoparticles compared to *C* and *n*. Size of APD deposited nanoparticles was also influenced by the nature of evaporating materials and substrates.

1. Introduction

Recently, arc plasma deposition (APD) is drawing considerable interest for depositing catalyst nanoparticles of several nm in size via direct and dry processes [1–3]. This technique directly evaporates a solid metal target into highly ionized plasma pulse in vacuum environment. The plasma pulse includes ample amount of nanoparticles with short pulse duration (<1 ms). Originally, this technique was applied for preparation of multilayers of nm thick layers with excellent interfacial properties [4]. In APD, deposited amount of nanoparticles can be easily and accurately controlled. Therefore, this technique can be applied for preparation of ample amount of individual nanoparticles on suitable catalyst support materials such as alumina and titania by controlling the number of plasma pulses before forming a complete layer. It is a simple and dry process without using complicated wet-chemical processes such as washcoating. Some promising results are coming out for catalyst applications and more [1–9]. Some aspects of deposition behavior of APD nanoparticles vs APD parameters have been studied [2–8]. However, many of deposition characteristics are still poorly understood or unknown, such as how small deposited nanoparticles can go and crystalline structures of APD deposited nanoparticles. In order to gain basic understanding of the APD process and control over the loading behavior, coverage, and maximize catalyst performance, systematic studies on the deposition characteristics of arc plasma generated nanoparticles are essential.

In this study, we show that ultra-small (<2 nm) nanoparticles of platinum and gold can be readily obtained by APD. In a series of systematic deposition of nanoparticles, we characterized average size and coverage of deposited nanoparticles of platinum and gold on two dimensional model substrates and identified the most sensitive APD parameter for controlling size and coverage of APD nanoparticles. During the process, controllable parameters were the discharge condenser voltage *V*, the discharge condenser capacity *C*, and the number of plasma pulse shots *n*. Amorphous carbon and titania films were used as model catalyst support.

2. Experimental

2.1. Model catalyst support preparation

Amorphous carbon films (~40 nm) were prepared on mica by thermal evaporation in a carbon coater. In the coater, a carbon rod was resistively heated to evaporate carbon atoms under 10^{-4} Torr vacuum. Amorphous titania films (~40 nm) were prepared on NaCl crystal using a flow type atomic layer deposition (ALD). Two precursors (titanium tetraisopropoxide [$Ti(OCH(CH_3)_2)_4$] as a metal precursor and H_2O as an oxidizing agent) were sequentially introduced into the chamber. Substrate was exposed to TTIP and H_2O for 30 and 10 s at working pressures of 0.25 and 0.1 Torr, respectively. Titania growth by ALD is self-limiting, as only precursor molecules chemisorbed on the surface can participate in film

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growth. High purity N_2 (99.999%) gas was used as the carrier and purging gas. During ALD, the base pressure was maintained below <5 m Torr. The sample was kept at 150 °C during titania deposition, the TTIP bottle at 50 °C, and the water was at room temperature.

2.2. Arc plasma deposition

Platinum and gold nanoparticles were deposited onto model catalyst support films by a coaxial pulsed arc plasma deposition (APD) system (ULVAC, ARL-300) at room temperature under 10^{-5} Torr vacuum [10]. In an APD system, a cylindrical cathode rod made of target materials (Pt or Au) and a trigger electrode is placed at the center and a cylindrical anode is coaxially mounted, wrapping the cathode [11]. A defined amount of charge is stored in a discharge condenser that is connected to cathode. When a trigger pulse induces an arc discharge between the surface of target rod (cathode) and anode, accumulated charge flows from a cathode spot to anode via an arc for a short time, typically less than 1 ms [11]. During the process, the cathode spot temperature rises more than tens of thousands degrees Celsius, vaporizing the cathode material and generating ionized plasma pulse with high kinetic energies (10 km/s) [12]. Right after discharge, the condenser is quickly charged up again for the next plasma pulse generation. During the process, controllable parameters are the discharge condenser voltage V, the discharge condenser capacity C, and the number of plasma pulse shots n.

2.3. TEM observation

After nanoparticle deposition, carbon films on mica were detached from mica by immersing the sample pieces in DI water. Upon contact with water, carbon films were detached from mica surface and afloat on water surface. Regular TEM grids were used to lift up the floating carbon films. Lifted carbon films on TEM grids were observed by TEM. Titania films on NaCl crystals were also immersed in water. Once supporting NaCl crystals were dissolved, titania films were afloat on water surface, lifted up by regular TEM grids, and brought to TEM for observation. TEM investigations were performed using a JEM 2100F (JEOL Co.) electron microscope with 2 Å point-to-point resolution and with acceleration voltage of 200 kV.

2.4. Image analysis

For measuring coverage and size distribution of deposited nanoparticles, ImageJ from NIH was used. Average particle sizes were calculated from the size of 50–150 individual particles and shown with standard deviation. Coverage values were estimated to have about ±5% deviation from the measured values due to the uncertainty in the measurement.

3. Results and discussion

3.1. Average particle size and coverage dependence on n

First we measured average particle size and coverage change of deposited nanoparticles with increasing number of plasma pulses n. Pt nanoparticles were deposited on amorphous carbon films on mica. Fig. 1 shows distributions of deposited Pt nanoparticles with 2, 5, and 10 plasma shots. The arc discharge condenser capacity C was 1080 μF and the arc discharge voltage V was 100 V. Fig. 1(a) shows blank carbon film without any deposition for comparison. Figs. 1(b)–(d) show deposited Pt nanoparticles as dark spots. With only 2 plasma pulses, individual Pt nanoparticles were readily observed (Fig. 1(b)). The average size of individual particles was 0.9 ± 0.2 nm. This size can be considered as intrinsic size of particles in generated plasma pulse as it was obtained with 2 plasma pulses only.

With increasing number of plasma pulses, average particle size increased (5 shots: 1.1 ± 0.2 nm, 10 shots: 2.4 ± 0.5 nm). Each plasma pulse shot is an independent event and incoming nanoparticles have narrow size distribution (Fig. 1(b)). If we assume that deposited nanoparticles remain on the impact spot, random collision of incoming nanoparticles in the next pulse shot with already deposited nanoparticles will cause the average particle size grow bigger due to coalescence upon collision. Of course, in reality, deposited particles can diffuse around as they will have excessive energy from their kinetic energies after thermal dissipation. How many of deposited particles or how far they can diffuse away will be dependent on the bonding strength between deposited nanoparticles and substrate. This effect will be discussed later.

With more plasma pulse shots, individual nanoparticles were eventually connected to each other, forming continuous films. Complete coverage was reached with about 80 plasma pulses (Fig. 2). Fig. 2(a) shows that deposited Pt nanoparticles were still isolated with 20 plasma pulses. Film formation was already substantial with $n = 40$ as shown in Fig. 2(b). In the figure, the dark area is deposited Pt, and scattered bright spots are empty spots not covered by Pt. With $n = 60$, empty spots are hardly seen, indicating that the film formation is nearly complete (Fig. 2(c)). Fig. 2(d) shows coverage development as a function of n. In the graph, the coverage increased linearly with n up to $n \sim 30$. For $n > 30$, coverage increase was not linear with n anymore. If it were linear, complete Pt film formation would have occurred with $n \sim 45$ as indicated by a dotted guideline in the graph. This slow down in coverage increase was due to local multilayer formation of deposited Pt. For each plasma pulse, Pt nanoparticles were randomly deposited. Therefore, as the coverage increased, more and more Pt nanoparticles were deposited on top of already deposited Pt and formed local multilayers. They did not diffuse around to fill the empty area in the film, not contributing to coverage increase. Those locally formed multilayers were imaged darker in the TEM images. One example is Fig. 2(c). Only when deposited Pt nanopaticles landed on the empty spots, they filled the hole in the film and increased the coverage. Therefore, complete film formation was delayed and reached only with $n \sim 80$.

3.2. Coverage dependence on arc discharge voltage V and condenser capacitance C

Fig. 3 shows particle size and coverage dependence on arc discharge voltage V. As V increased from 70 V to 300 V, particle size and coverage increased drastically. Here, the number of plasma pulses n was two and condenser capacitance C was 1080 μF. Average particle size for the 200 V deposition was 1.9 ± 0.4 nm, about two times bigger than that of the 100 V deposition (0.9 nm). For comparison, the average particle size for the 200 V deposition was smaller than that of Fig. 1(d) with 10 pulse shots with 100 V, but the coverage was almost the same (21% vs 22%). This observation shows that two times higher V (from 100 V to 200 V) with the same n yielded almost the same amount of deposited particles as that of five times more pulses (2 pulses vs 10 pulses) with the same V. Deposited amount increased much faster when we increased V to 300 V. Coverage increased about 15 times with 3 times higher V from 100 V to 300 V (Fig. 3(c)). With $V = 300$ V, deposited particles were not individual anymore and connected to each other. In other words, increasing V was much more efficient for increasing the amount (= coverage) of deposited nanoparticles than increasing the number of plasma pulses n. Guideline in Fig. 3(d) is in the form of $y = Ax^3$ (with 0 intercept at y axis), showing that the coverage increased with the third degree of V.