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Abstract	<p>In this chapter, we discuss the most recent advances in the preparation of nanocatalysts via dry processes. We describe the fabrication of metal nanoparticles using lithography and the synthesis of catalytic nanoparticles using non-colloidal techniques, including plasma deposition and lithographical techniques. Synthesis of oxide-supported metal catalysts via wet-chemical processes is well known in heterogeneous catalysis [1–3]. Impregnation, coprecipitation, deposition-precipitation, ion exchange, sol–gel, and colloidal processes are typical examples of wet processes. Typically, precursors of the active catalyst materials are dissolved and reacted in an aqueous or organic solution and the solution is mixed with ceramic supports to prepare the</p>	

oxide-supported metal catalysts. In general, the wet-chemically produced oxide-supported metal catalysts need to undergo annealing processes at elevated temperature in order to eliminate the organic materials required for the wet processes, such as solvent, surfactant, or capping agents [4–6]. The annealing process can cause oxidation of the catalyst metal particles, causing catalytic activity deterioration. In order to overcome the shortcomings of wet-chemical processes, direct vaporization of metallic materials to deposit active materials on ceramic supports has drawn considerable interest due to its simplicity, high reproducibility, and the possibility for large-scale production. Examples of such dry synthesis processes for nanocatalyst production are arc plasma deposition (APD) [7–9], e-beam lithography [10, 11], and laser vaporization [12, 13]. In this chapter, we introduce APD and nanolithography technologies for preparing catalyst materials and discuss recent advances in their application.

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# Chapter 3

## Non-colloidal Nanocatalysts Fabricated with Nanolithography and Arc Plasma Deposition

Sang Hoon Kim and Jeong Young Park

### 3.1 Introduction

In this chapter, we discuss the most recent advances in the preparation of nanocatalysts via dry processes. We describe the fabrication of metal nanoparticles using lithography and the synthesis of catalytic nanoparticles using non-colloidal techniques, including plasma deposition and lithographical techniques. Synthesis of oxide-supported metal catalysts via wet-chemical processes is well known in heterogeneous catalysis [1–3]. Impregnation, coprecipitation, deposition-precipitation, ion exchange, sol–gel, and colloidal processes are typical examples of wet processes. Typically, precursors of the active catalyst materials are dissolved and reacted in an aqueous or organic solution and the solution is mixed with ceramic supports to prepare the oxide-supported metal catalysts. In general, the wet-chemically produced oxide-supported metal catalysts need to undergo annealing processes at elevated temperature in order to eliminate the organic materials required for the wet processes, such as solvent, surfactant, or capping agents [4–6]. The annealing process can cause oxidation of the catalyst metal particles, causing catalytic activity deterioration. In order to overcome the shortcomings of wet-chemical processes, direct vaporization of metallic materials to deposit active materials on ceramic

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supports has drawn considerable interest due to its simplicity, high reproducibility, and the possibility for large-scale production. Examples of such dry synthesis processes for nanocatalyst production are arc plasma deposition (APD) [7–9], e-beam lithography [10, 11], and laser vaporization [12, 13]. In this chapter, we introduce APD and nanolithography technologies for preparing catalyst materials and discuss recent advances in their application.

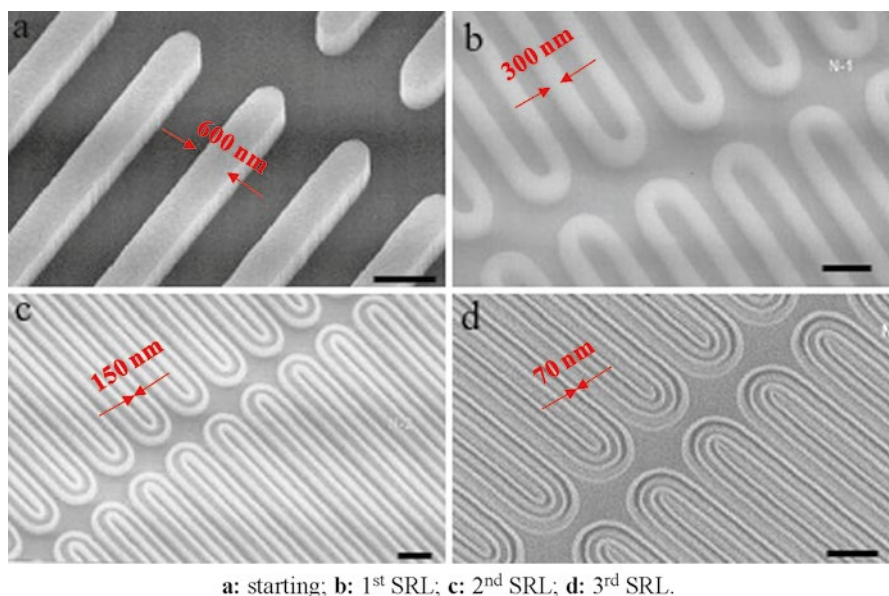
## 3.2 Nanocatalysts Fabricated with Lithography

### 3.2.1 Nanolithography for Fabrication of Nanodots and Nanowires

Lithography-based nanocatalyst fabrication is one of the main techniques developed for the production of catalysts with high throughput [14–16]. It has the advantage of precise control of particle size and inter-particle distance. The two-dimensional (2D) array of nanocatalysts produced via lithography is also highly monodispersed. Lithography-based nanocatalysts can be formed on any substrate; therefore, it can form a controlled oxide–metal interface, which offers opportunities for studying the role of the interface between the catalytically active phase and the support in catalytic reactions. Moreover, a fabricated 2D array of nanodots or nanowires can be easily cleaned and crystallized for catalyst studies with various surface treatments.

Most importantly, the nanolithography routes exemplified in this section are applicable to the fabrication of any other 2D nanocatalysts on different substrates. The simplest route is electron beam lithography (EBL) [17–19], which utilizes high-resolution pattern writing with a focused electron beam, followed by electron-sensitive resist/etching. It can fabricate nanoparticles with a size of ~10 nm. However, nanofabrication with EBL is limited by low throughput and high cost. A new method called size reduction lithography (SRL) [20] can reduce the mold from 0.6  $\mu\text{m}$  polysilicon to ~7 nm silicon nanowire. The nanowire pattern is transferred into polymethyl methacrylate (PMMA) under high pressure and high temperature using nano imprint lithography (NIL). A thermal oxide layer formed by oxygen-plasma etching upon the residual PMMA is then removed. In this way, a nanoscale mold is fabricated. Figure 3.1 presents the multiplication of pattern density by SRL. Pt atoms can be deposited by electron beam evaporation to form Pt nanowires. Thermal treatment in vacuum, hydrogen, or oxygen crystallizes the Pt nanowires [21, 22]. The major contaminant, carbon from PMMA, can be removed by thermal oxidation under low pressure ( $1 \times 10^{-6}$  Torr) of  $\text{NO}_2$  at 573 K. The adsorbed oxygen remaining after the carbon removal step can be removed by converting CO into  $\text{CO}_2$ .

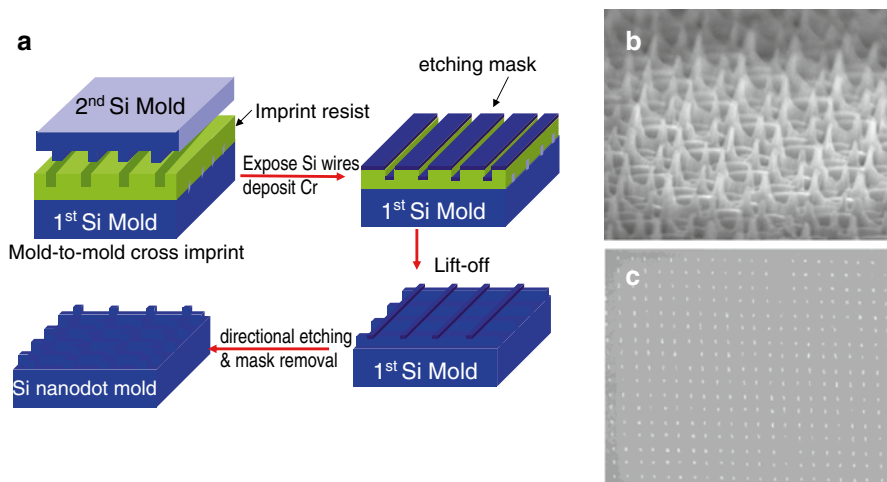
Another method for fabricating catalytic nanodots is called mold-to-mold cross imprint (MTMCI) [24]. This technique is capable of producing high areal density nanodots of any metal on any surface. It includes three main steps. First, a silicon



a: starting; b: 1<sup>st</sup> SRL; c: 2<sup>nd</sup> SRL; d: 3<sup>rd</sup> SRL.

**Fig. 3.1** Multiplication of pattern density by size reduction lithography. (a) After patterning a sacrificial poly-Si layer; (b) after SiO<sub>2</sub> deposition, a SiO<sub>2</sub> spacer etch by CF<sub>4</sub> plasma, and removal of the sacrificial poly-Si by KOH; (c) after poly-Si deposition, poly-Si spacer etch by Cl<sub>2</sub> and HBr, and removal of SiO<sub>2</sub> by HF; and (d) after SiO<sub>2</sub> deposition, SiO<sub>2</sub> spacer etch by CF<sub>4</sub> plasma, and removal of sacrificial poly-Si by KOH. Thus, 8 (=23) lines with a line width of 70 nm and interline spacing of 80 nm were generated after threefold reduction lithography. The scale bars in all images are 1  $\mu$ m. Reprinted with permission from ref. [23]. Copyright Springer

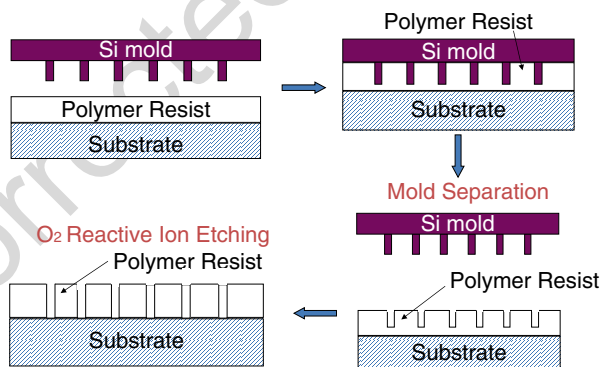
wire mold is fabricated using spacer lithography. Second, a MTMCI technique is used to convert the silicon spacer nanowires into silicon nanopillars. The principle of the second step is to pattern a silicon spacer nanowire mold with another nanowire mold by imprinting one mold placed perpendicularly onto the other. Figure 3.2a shows the protocol for the fabrication of a silicon nanodot model using the MTMCI technique. In the second step, an array of silicon nanopillars is fabricated at the intersection of the silicon and chromium nanowires by etching the silicon. The silicon nanopillars thus formed have a size of 15  $\times$  30  $\times$  250 nm. Figure 3.2b is an array of silicon nanopillars, which acts as the final mold for the fabrication of the 2D catalytic nanodots on the substrate. The third step is the imprinting of the Pt nanodots (Fig. 3.3). The silicon nanopillar mold is imprinted into a PMMA layer on silicon oxide layers formed naturally on a commercially available silicon wafer. A thin layer of Cr is deposited via angled evaporation as a hard mask for the PMMA mold. Then, Pt atoms are deposited into the uncovered nanowell, forming Pt nanodots with dimensions of 15  $\times$  30  $\times$  5 nm. Figure 3.2c is an array of Pt nanodots on silicon oxide after removal of the residual PMMA. Compared to the cleaning and crystallization of Pt nanowires fabricated through SRL, similar cleaning routes [21, 22] are used for cleaning and crystallization of the Pt nanodots.



**Fig. 3.2** (a) Scheme of mold-to-mold cross imprint (MTMCI) to fabricate a nanopillar mold. (b) SEM of a nanopillar mold (each nanopillar:  $15 \times 30 \times 250$  nm). (c) A homogeneous array of Pt nanodots (each nanodot:  $15 \times 30 \times 5$  nm) made by MTMCI. Reprinted with permission from ref. [23]. Copyright Springer

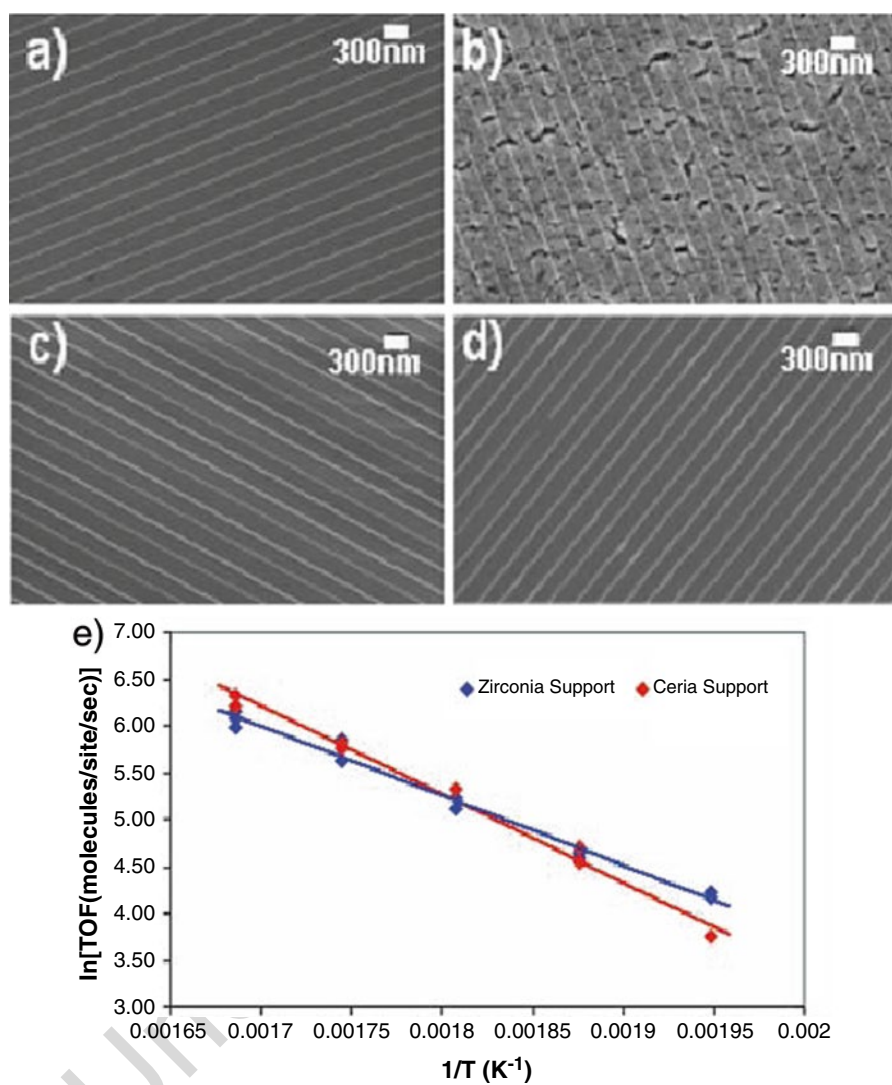
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**Fig. 3.3** Scheme of nanoimprint lithography. Reprinted with permission from ref. [23]. Copyright Springer



### 3.2.2 Catalytic Properties of Nanowires Fabricated with Lithography

Dense arrays of platinum nanowires deposited on the oxide thin-film surfaces of  $\text{ZrO}_2$ ,  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{CeO}_2$  are fabricated by combining lithographic nanofabrication and nanoimprint technology [16]. These nanowire arrays have been used to study the effects of oxide support on the catalytic oxidation of CO. Figure 3.4 shows



**Fig. 3.4** SEM images of 20-nm wide Pt nanowires on different oxide supports. All wires are 5 nm in height. (a) Silica support; (b) ceria support; (c) alumina support; (d) zirconia support. (e) Arrhenius plots measured for CO oxidation reactions on zirconia- and ceria-supported Pt nanowire arrays. Reprinted with permission from ref. [16]. Copyright Springer

SEM images of the nanowire arrays on different oxides. From the SEM images, the typical dimensions of a single platinum nanowire are  $20 \times 5 \times 12$  nm (width  $\times$  height  $\times$  length). Catalytic oxidation of CO to  $\text{CO}_2$  over the various catalyst arrays was carried out in temperatures of 513–613 K. Figure 3.4e shows Arrhenius plots for the reaction on zirconia- and ceria-supported samples. Apparent activation

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energies for the zirconia- and ceria-supported wire arrays are  $14.6 \pm 0.2$  and  $18.8 \pm 0.2$  kcal/mol, respectively. The nanowires on silica have an activation energy of  $12.6 \pm 0.2$  kcal/mol. Therefore, the nanocatalysts composed of metal nanowires and oxide supports reveal support dependence for both reaction turnover frequency (TOF) and the measured activation energy.

### 3.3 Nanocatalysts Fabricated Via Arc Plasma Deposition

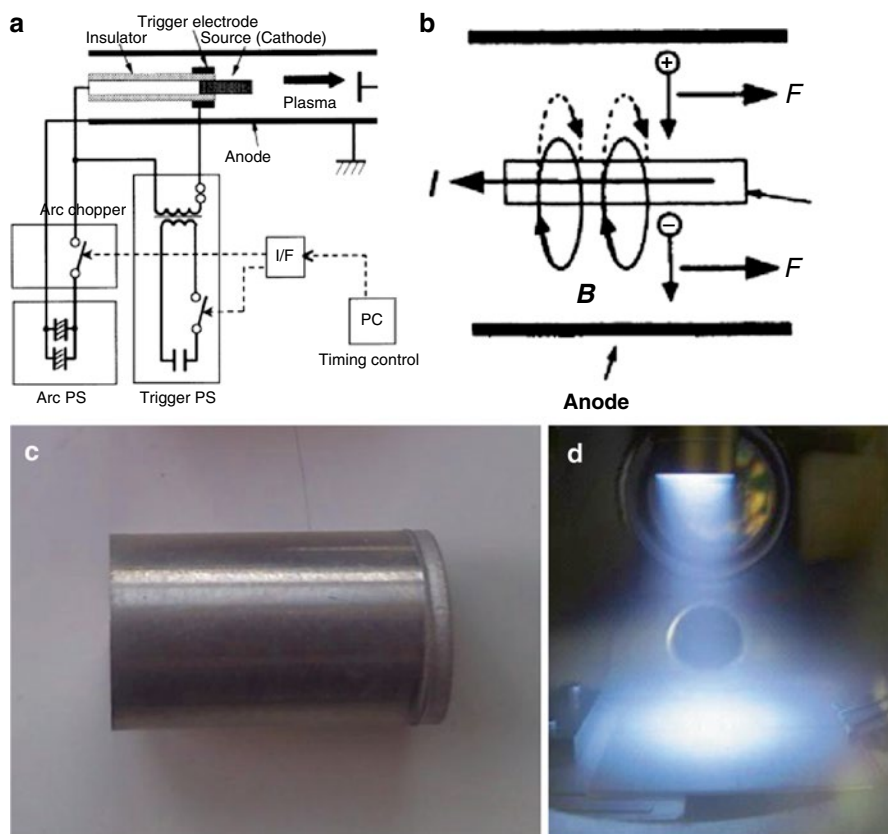
#### 3.3.1 Introduction to Arc Plasma Deposition

APD, or cathodic arc deposition, has been traditionally applied when preparing dense thin films of corrosion-resistant, protective, and decorative coatings, such as TiN, TiC, and CrN [25–27]. This method is usually regarded as physical vapor deposition (PVD), but it differs from other PVD methods in that energetic plasma ions condense to form dense films in APD, while in other PVD methods, it is the vapor of neutral atoms that condense [25].

In APD, very high current densities ( $\sim 10^{12}$  A/m<sup>2</sup>) let the cathode material directly evaporate from the surface. A plasma discharge then generates cathodic arcs within the vapor. The size of arc spot is typically a few microns [26]. The plasma generated at arc spots expands rapidly into the ambient vacuum. The final velocities of the generated ions are  $\sim 1\text{--}2 \times 10^4$  m/s and are largely independent of the cathode materials. These velocities correspond to the kinetic energies of about 20 eV for light elements and 200 eV for heavy elements [25]. The biggest obstacle of implementing the APD method has been that macrodroplets are also emitted simultaneously from the cathode spot along with the plasma ions and electrons. The droplets adhere to the film and act as defects. Another problem of the APD method is that it is not easy to control the arc generation location [28, 29]. In order to reduce or eliminate macrodroplets, various methods have been tried, such as steered arc [30], distributed arc [31], and filters [28, 32, 33].

Among these trials, pulsed coaxial APD offers macrodroplet-free plasma deposition without large-scale conventional magnetic filter systems in the vacuum chamber. Chun et al. developed the pulsed coaxial APD system shown in Fig. 3.5a [34]. A high-voltage pulse (a few kilovolts, tens of microseconds) is applied between the trigger and cathode cylinder. This voltage induces dielectric breakdown and trigger discharge. Then, the main discharge occurs sequentially between the cathode spot and the cylindrical anode, where a voltage of 50–300 V is applied. During arc discharge, a very large current ( $\sim 2,000$  A) flows through the cathode (Fig. 3.5b). Due to the large magnetic field induced by the current, plasma ions and electrons fly away from the cathode towards the substrate. Meanwhile, any macrodroplets, which are neutral, fly towards the anode and adhere to the anode surface. Because the duration of the arc is less than 1 ms, heating of the cathode material and generation of macrodroplets are minimized. As the arc plasma is generated between the cathode





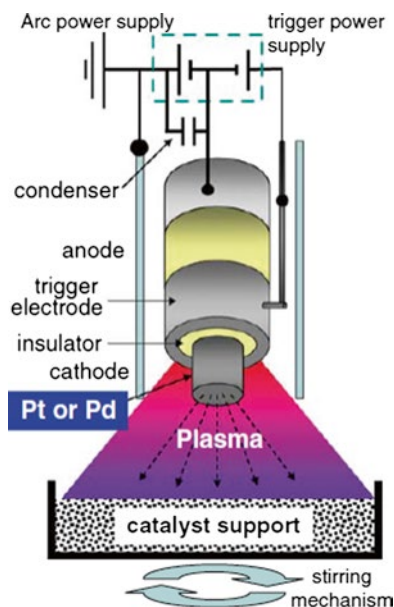
**Fig. 3.5** Schematic diagram of (a) coaxial pulsed arc plasma deposition system and (b) quasi-stationary model of a generated arc plasma.  $I$  is the arc current,  $B$  is the magnetic field induced by  $I$ , and  $F$  is the electromagnetic force applied to the plasma ions and electrons. Reprinted with permission from ref. [34]. Copyright 2000 Elsevier Science S.A. (c) Used cathode cylinder made of palladium. The plasma is generated from the circular rim on the right side. (d) A generated arc plasma. The plasma beam accelerates towards bottom of the image. Courtesy of Ulvac-Riko, Inc.

and anode surfaces, arc spots are limited to the protruded rim of the cathode cylinder. For example, a slightly used cathode cylinder is shown in Fig. 3.5c. In the figure, the rim on the right is used for plasma generation. Therefore, by controlling the length of the protrusion, arc spots can be limited to the rim of the protrusion. Figure 3.5d shows an actual arc plasma beam generated from the cathode (top). The accelerated plasma beam hits the bottom, where catalyst support materials are placed. In the case of powder-type catalyst supports, the powder is constantly stirred for effective dispersion of the deposited catalyst nanoparticles on the powder. In case of thin-film-type catalyst supports, no stirring is needed.

This pulsed coaxial APD has been used to fabricate multilayer structures with sub-nanometer thickness control [34–36] without the need of filters, such as curved

**Fig. 3.6** Schematic of arc plasma deposition of nanoparticles on a catalyst support.

In the case of powder-type catalyst supports, the powder is constantly stirred for effective dispersion. In the case of thin-film-type catalyst supports, no stirring is needed. Reprinted with permission from ref. [38]. Copyright 2009 Springer Science + Business media, LLC

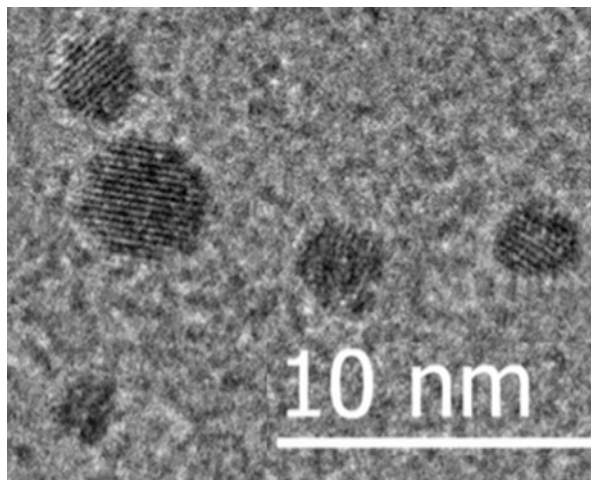


ducts, to remove macrodroplets [37]. Another advantage of pulsed coaxial APD is that each pulse generates a very large number of nanoparticle ions a few nanometer in size ( $\sim 1\text{--}5$  nm). The amount of deposited materials or, for the two-dimensional case, coverage of the deposited materials can be easily controlled by the number of pulses.

As long as the material is solid and can be formed as a cylindrical cathode target for an APD system, any material can be dry-deposited as nanoparticles without going through wet-chemical processes. Those deposited nanoparticles can be used as seed particles for growing nanotubes [39, 40] or for decorating underlying nanostructures to form complex nanocomposites with enhanced functionalities [41]. Among these new possibilities, using APD to dry deposit nanoparticles as nanocatalyst materials have drawn significant attention and interest is rapidly growing [42]. Figure 3.6 shows a schematic of depositing catalytic nanoparticles on catalyst supports. It is a dry process in a high vacuum chamber with a base pressure of  $\sim 10^{-7}$  Torr. Nanoparticles generated from the cathode surface are accelerated towards the bottom due to the high magnetic field induced by the high current flowing along the cathode axis, as discussed above.

Figure 3.7 shows a TEM image of individual Pt nanoparticles deposited by APD on an amorphous carbon film substrate. The dark dots are Pt nanoparticles and the gray background is the amorphous carbon substrate. The nanoparticles are  $\sim 1\text{--}5$  nm in size and lattice structures are clearly seen in the particles. In the following sections, recent applications of APD for nanocatalyst preparation are discussed.

**Fig. 3.7** Arc plasma-deposited Pt nanoparticles on amorphous carbon



### 3.3.2 Nanocatalysts on Two-Dimensional Supports Using APD

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As a model for metal-oxide hybrid catalysts using strong metal-support interactions (SMSI) [43], thin-film-type substrates have been employed to disperse catalyst nanoparticles [44–46]. Recently, Qadir et al. compared the catalytic activity of Pt nanoparticles prepared by conventional wet-chemistry methods and by APD on TiO<sub>2</sub> thin film substrates [9]. In the study, ~150 nm thick TiO<sub>2</sub> films were sputtered on Si wafers and used as catalytic supports. Approximately the same amount of Pt (0.12 mg) was deposited using APD (150 pulses, arc discharge voltage 100 V, discharge condenser capacity 1,080 μF) and conventional impregnation. For impregnation, potassium hexachloroplatinate (K<sub>2</sub>PtCl<sub>6</sub>) was dissolved in distilled water and droplets were dropped and dried, then the sample was annealed at 500 °C for 5 h to remove organic substances. The catalytic activity was tested using CO oxidation in an ultra-high-vacuum (UHV) batch reactor. As can be seen in Fig. 3.8, the catalytic activity of the dry-deposited Pt nanoparticles on the TiO<sub>2</sub> films was higher than that of the impregnated ones. The 150-pulse APD Pt was enough to have 100 % surface coverage. Therefore, it was assumed that the deposited Pt is thicker than one monolayer and that the layer is flat. From these assumptions, the number of active sites on the deposited Pt layer was calculated, and the turnover frequency (TOF) (Fig. 3.8a) and activation barrier for the reaction (Fig. 3.8b) were measured.

Still, it is not easy to find clues for the observed difference in catalytic activities from only these structural aspects. The XPS analysis in Fig. 3.9 shows that the impregnated and annealed Pt nanoparticles have inactive bulk oxide states, while the APD Pt nanoparticles are purely metallic. This oxide formation during annealing is considered the main reason for the difference in the catalytic activities. In order to improve catalytic activity, impregnated and annealed Pt nanoparticles on TiO<sub>2</sub> films were reduced under 100 Torr of hydrogen at 250 °C for 1 h to decrease the oxidation state. However, the catalytic activity after reduction was still lower than that of the

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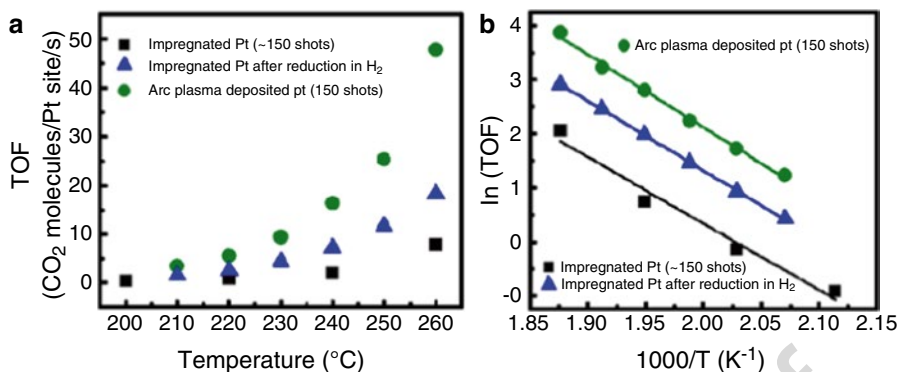
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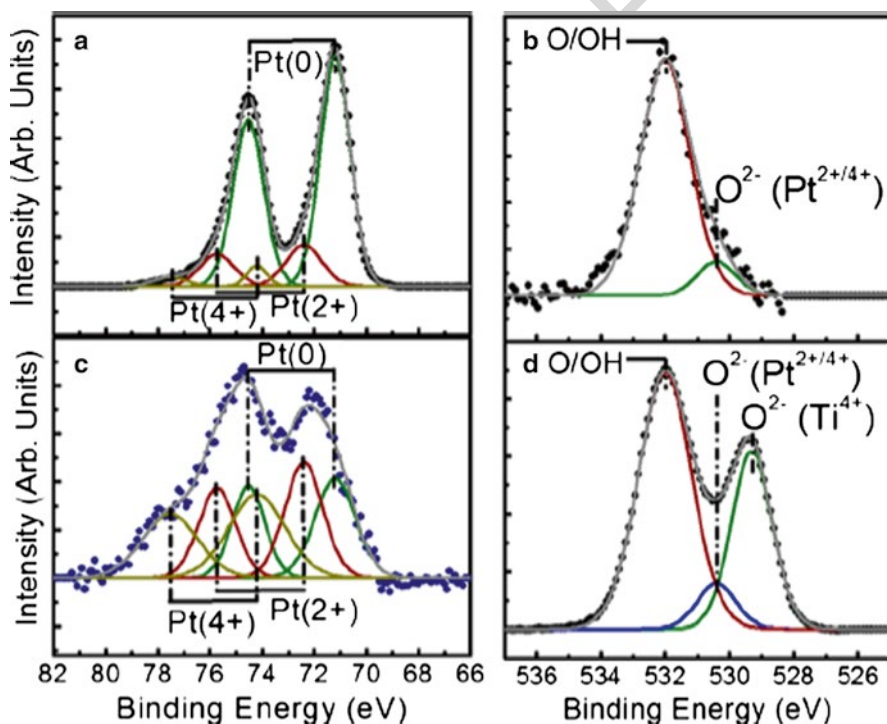
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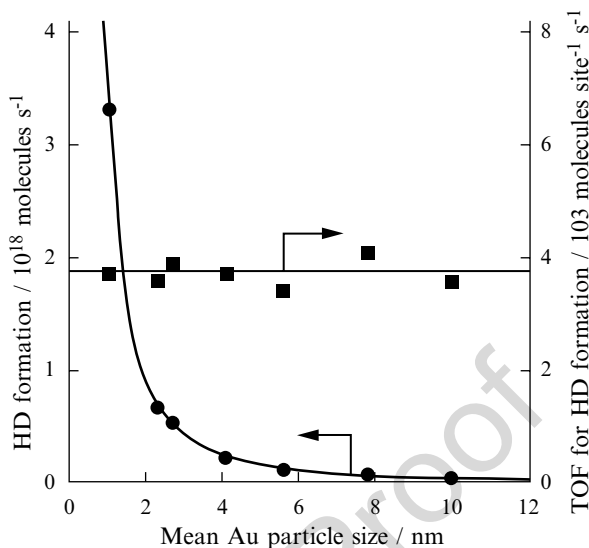


**Fig. 3.8** Comparison of the catalytic activity of Pt nanoparticles on TiO<sub>2</sub> films prepared by APD and impregnation. Reprinted with permission from ref. [9]. Copyright 2012 American Chemical Society



**Fig. 3.9** XPS measurement of (a) Pt 4f and (b) O 1s peaks of 150 pulse APD Pt nanoparticles and (c) Pt 4f and (d) O 1s peaks of a similar amount of impregnated and annealed Pt nanoparticles on TiO<sub>2</sub> films. Reprinted with permission from ref. [9]. Copyright 2012 American Chemical Society

**Fig. 3.10** Comparison of the HD formation rates vs. mean gold particle size for the same amount of deposited gold on TiO<sub>2</sub>(110). Reprinted with permission from ref. [47]. Copyright 2009 Wiley-VCH Verlag



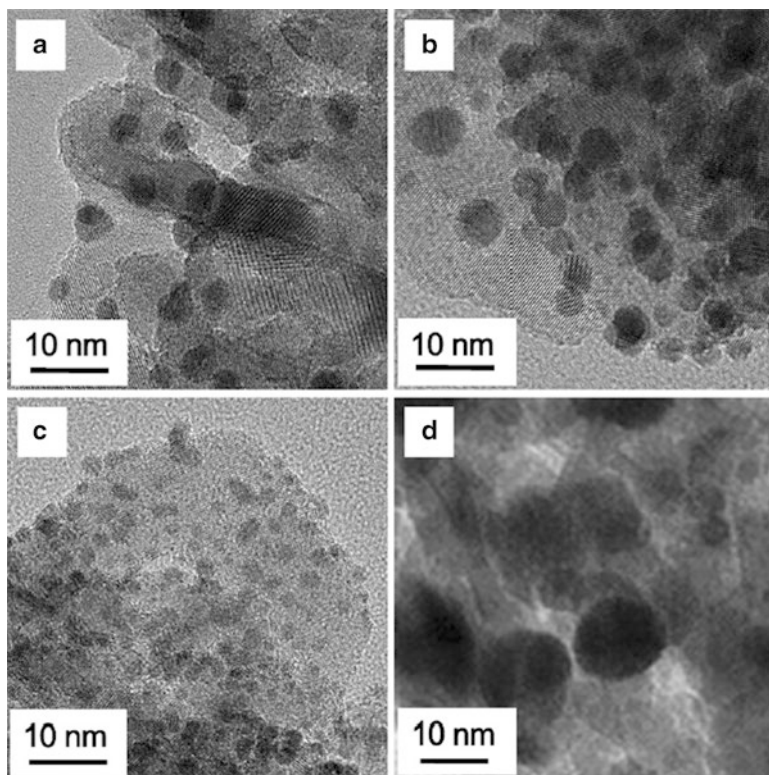
APD Pt nanoparticles (Fig. 3.9a). Furthermore, XPS survey spectra showed a very small peak for K on the impregnated Pt nanoparticles. The presence of K ion may have blocked active sites too [9]. This study showed that APD enabled the deposition of metallic Pt nanoparticles on TiO<sub>2</sub> films with neither oxidation due to annealing nor impurities commonly found in conventional wet-chemical processes.

Fujitani et al. examined hydrogen molecule dissociation at low temperature (425 K) on gold nanoparticles deposited on TiO<sub>2</sub>(110) single crystal surface via APD [47]. In the study, they deposited the same amount of gold nanoparticles with average diameters of ~1–10 nm by changing the discharge condenser capacity between 360 and 2,200  $\mu$ F. They then exposed the prepared Au/TiO<sub>2</sub>(110) surface to the H<sub>2</sub> and D<sub>2</sub> exchange reaction and measured the rate of HD formation (Fig. 3.10). The rate of HD formation increased dramatically when the gold particle size was below 2 nm, while the TOF was more or less constant over the entire particle size range. TOFs were calculated by dividing the number of HD molecules formed per second by the total number of gold atoms at the periphery of the gold particles. Based on this measurement, the active sites for H<sub>2</sub> dissociation are along the periphery around the deposited gold particles. This study shows that it is possible to control the size of nanoparticles generated by APD in the nanometer range by controlling the parameters for arc plasma generation.

### 3.3.3 Nanocatalysts on Three-Dimensional Supports Using APD

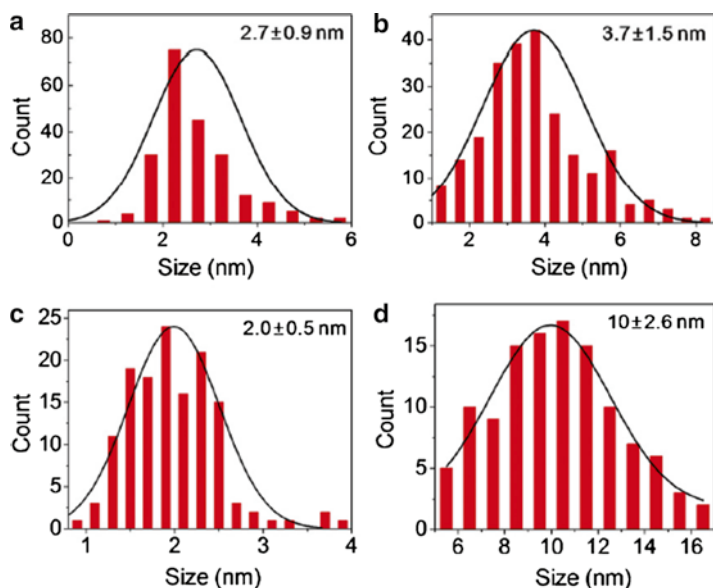
For a two-dimensional substrate, we can assume the number of active sites or directly measure the coverage of catalyst particles. Therefore, quantitative analysis





**Fig. 3.11** TEM images of APD-deposited gold and platinum nanoparticles on TiO<sub>2</sub> powder. The arc discharge condenser capacity was 1,800  $\mu$ F. (a) Au/TiO<sub>2</sub> at discharge voltage of 200 V, (b) Au/TiO<sub>2</sub> at discharge voltage of 300 V, (c) Pt/TiO<sub>2</sub> at discharge voltage of 200 V, and (d) Au/TiO<sub>2</sub> prepared by sol-gel method for comparison. Reprinted with permission from ref. [8]. Copyright 2013 Elsevier Science S.A.

(e.g., TOF and active barrier calculations) is possible, as shown in the previous section, and two-dimensional substrates can be used as model catalyst supports. On the other hand, three-dimensional powder supports are much more widely used in industry, but it is not easy to do quantitative analysis using a powder support. Still, it is important to improve processes to incorporate catalyst nanoparticles on powder support, such as better dispersion of ever smaller nanoparticles or controlling the adhesion strength between catalytic nanoparticles and support powder materials. Recently, Kim et al. studied the catalytic activity of nanometer-sized Au and Pt particles deposited on TiO<sub>2</sub> powder via APD [8]. In the study, they controlled the size of the deposited nanoparticles by changing the arc discharge voltage,  $V$ , for generating plasma. Figures 3.11 and 3.12 show TEM images and the size distribution of the APD-deposited Au and Pt nanoparticles on TiO<sub>2</sub> powder, respectively. The metallic nanoparticles are seen as dark spots, while the catalyst support TiO<sub>2</sub> powder particles are seen as bright and extended shapes. Nanoparticles deposited by



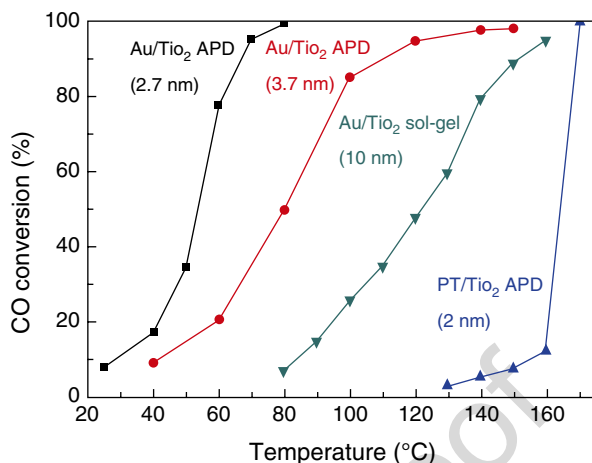
**Fig. 3.12** Particle size distributions of the Au/TiO<sub>2</sub> and Pt/TiO<sub>2</sub> particles shown in Fig. 3.9. (a)–(d) corresponds to those in Fig. 3.9. Reprinted with permission from ref. [8]. Copyright 2013 Elsevier Science S.A.

APD tend to increase in size with increasing  $V$ ; this tendency can be seen in Fig. 3.11a, b. Although prepared using the same deposition conditions, the Au and Pt nanoparticles had different sizes (Fig. 3.11a, c). Figure 3.11d shows nanoparticles prepared using the wet-chemical sol–gel method for comparison. The sol–gel-prepared nanoparticles are ~10 nm in size—bigger than those prepared by APD, which are ~2–4 nm in size (Fig. 3.12).

Gold nanoparticles are well known for their high catalytic activity for CO oxidation [48, 49]. On the nanometer scale, the catalytic activity of gold nanoparticles increases with decreasing size [41, 50]. On the other hand, it is known that the catalytic activity of Pt nanoparticles is independent of particle size [49, 51]. The catalytic activity comparison for the samples shown in Fig. 3.13 reflects these tendencies. In the comparison, the overall CO oxidation efficiency followed the order of Au/TiO<sub>2</sub> 200 V > Au/TiO<sub>2</sub> 300 V > Au/TiO<sub>2</sub> sol–gel > Pt/TiO<sub>2</sub> 200 V. Regardless of preparation method, be it dry or wet, particle size is the most important parameter for the catalytic activity of nano-sized gold. On the other hand, Pt/TiO<sub>2</sub> 200 V had the lowest catalytic activity, as the catalytic activity was not very different from that of bulk Pt. The catalytic activity of gold increased with decreasing particle size and eventually surpassed Pt. Again, it was possible to control the size of the nanoparticles with the parameters for generating the arc plasma. However, it was within the same materials only. For different materials, the particles differed in size when using the same parameters for arc plasma generation.

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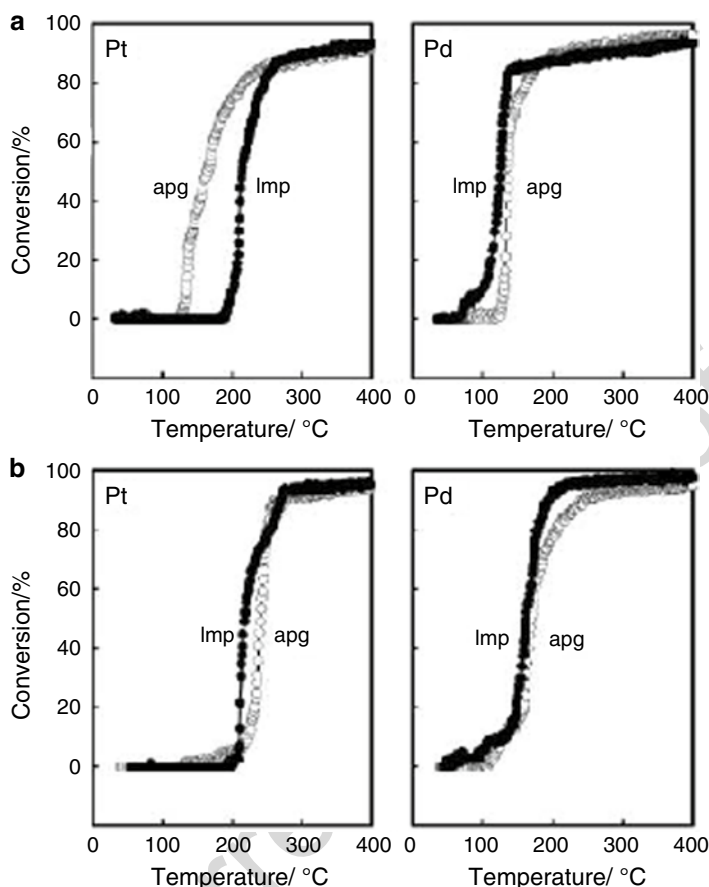
**Fig. 3.13** Catalytic activity comparison for Au/TiO<sub>2</sub> and Pt/TiO<sub>2</sub>. Reprinted with permission from ref. [8]. Copyright 2013 Elsevier Science S.A.



Hinokuma et al. reported a similar study on dispersing Pt and Pd nanoparticles on  $\gamma$ -alumina powder using APD and conventional impregnation. They compared the catalytic activities for CO oxidation [38]. In the study, they found out that the average size of the Pt nanoparticles deposited by APD is  $\sim 2.5$  nm and the size of the Pd nanoparticles is 6.8 nm. XPS measurements showed that the Pt nanoparticles were metallic regardless of the preparation method. As for the Pd nanoparticles, they were mostly in their oxide form (PdO) when prepared by impregnation. When prepared by APD, however, the metallic Pd had a higher fraction (60 %) than the Pd-oxide (40 %). As the APD process occurs in vacuum and directly vaporizes the metallic cathode materials, the deposited nanoparticles tend to be metallic. Figure 3.14 shows a comparison of the catalytic activities of Pt/alumina and Pd/alumina powders prepared by APD and impregnation. For comparison, they loaded the same amount (0.4 wt%) of Pt and Pd on  $\gamma$ -alumina powder and labeled “apg” for APD preparation and “imp” for impregnation. For the Pt/alumina samples, APD-prepared samples showed higher catalytic activity than impregnation-prepared samples due to their higher dispersion (Fig. 3.14a, left). However, after thermal aging in 10 % H<sub>2</sub>O/air at 900 °C for 25 h, deactivation was more pronounced for the APD-prepared samples than for the impregnation-prepared sample (Fig. 3.14b, left). This observation indicates that the thermal stability of APD-dispersed Pt nanoparticles on  $\gamma$ -alumina is not so good. With TEM, they actually observed sintering of Pt nanoparticles up to 20 nm in size. For the Pd/alumina samples, the situation was somewhat different. The APD-prepared samples showed a slightly lower catalytic activity than the impregnation-prepared samples (Fig. 3.14a, right). They explained this difference by the higher catalytic activity of PdO than metallic Pd [52].

Hinokuma et al. continued their study to include prepared bimetallic Pd-Fe nanoparticles on ceria powder using APD and investigated their catalytic activity for CO oxidation [53]. In the study, they prepared bimetallic nanoparticles using two plasma guns in a chamber, one for Pd and one for Fe. They prepared the

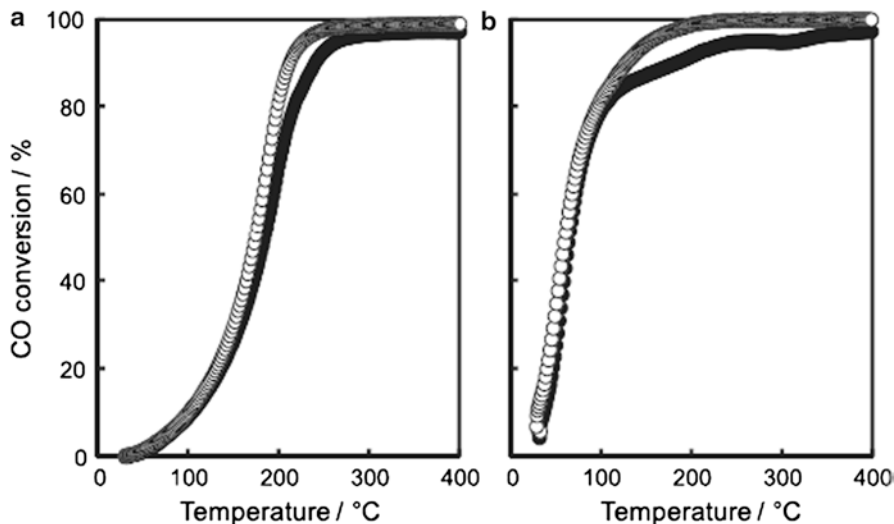




**Fig. 3.14** Catalytic activity comparison for Pt/alumina and Pd/alumina (a) as prepared and (b) after thermal aging. Reprinted with permission from ref. [38]. Copyright 2009 Springer Science+Business media, LLC

bimetallic nanoparticles using the two cathode guns synchronously (syn) and asynchronously (asyn). Synchronous pulses of Pd and Fe resulted in Pd-Fe bimetallic alloy nanoparticles, while asynchronous pulses resulted in individual Pd and Fe nanoparticles on the ceria support. They found out that Pd-Fe bimetallic nanoparticles showed slightly higher catalytic activity than the individual metal nanoparticles (Fig. 3.15a). They attributed these findings to better dispersion and a higher metallic fraction of Pd in the Pd-Fe alloy nanoparticles on ceria. The catalytic activity increased after thermal aging for both the synchronous- and asynchronous-prepared samples (Fig. 3.15b). The authors argued that, in contrast to the alumina case above, thermal aging helped stabilize the Pd–O–Ce bonding, keeping the dispersion of nanoparticles intact, which enabled higher catalytic activity after thermal aging [54].

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**Fig. 3.15** Comparison of catalytic activity for Pd-Fe on ceria powder by APD. (*Open circles*) Pd-Fe/ceria (syn) (*filled circles*) Pd-Fe/ceria (asyn), (**a**) before and (**b**) after thermal aging. Reprinted with permission from ref. [53]. Copyright 2013 Elsevier Science S.A.

### 3.3.4 Some New Applications for Nanoparticles Prepared Via APD

Other than the familiar gas-phase catalytic reactions, examples of APD-deposited nanoparticle applications in some new fields are also emerging. In order to investigate photocatalytic antibacterial effects, Oveisi et al. deposited silver nanoparticles on mesoporous anatase titania films using APD [55]. The size of the deposited nanoparticles ranged between 3.7 and 5.6 nm by changing the number of arc plasma pulses. When a droplet of *E. coli* suspension is dropped on top of Ag nanoparticles dispersed on titania and irradiated with UV light, the survival fraction of *E. coli* cells decreased as the nanoparticle size decreased. In other words, smaller Ag nanoparticles were more effective for inactivating the bacteria. For sensing applications, Ito et al. reported detection of hydrogen peroxide using APD-deposited Pt nanoparticles on carbon electrodes in an electrochemical setup [56]. In the study, they varied the coverage of the Pt nanoparticles on glassy carbon surfaces by incrementally increasing the number of plasma pulses from 5 to 20. The average particle size was 2.7 nm. After annealing the Pt-deposited glassy carbon, only the Pt nanoparticles deposited using five APD pulses remained as individual particles, while Pt particles deposited using more APD pulses coalesced to form connected island shapes. After annealing, electrodes with individual Pt nanoparticles showed better sensitivity than electrodes with connected Pt islands for hydrogen peroxide detection.

### 3.4 Summary and Outlook

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In this chapter, we have discussed the most recent advances in the preparation of catalyst nanoparticles on catalyst support using dry processes. These two-dimensional model catalyst arrays fabricated using nanolithography have been used to study the support dependence of CO oxidation reaction kinetics; they indicate that the most important factor affecting TOF is the interaction of the platinum and the support. The APD method was traditionally used for preparation of dense protective coating layers. However, with the advent of pulsed APD, new applications for preparing metallic nanoparticles in a direct and dry process are emerging. So far, applications are limited to the much studied gas-phase reactions—mostly the model CO oxidation reaction. However, we have also noticed that the scope of applications is widening, too (e.g., liquid-phase photocatalysts, electrode materials for fuel cells and secondary batteries, and sensor applications). The biggest advantage of APD is that it is relatively easy to generate a large amount of particles a few nanometer in size. It is also easy to control the size of the generated nanoparticles, on the nanometer scale, by controlling APD parameters, such as the number of arc plasma pulse shots, arc discharge voltage, and arc discharge condenser capacitance. As for substrates for deposition, the APD method provides a simple and easy method for direct and dry deposition of metallic nanoparticles on a variety of substrates, such as two-dimensional thin films and three-dimensional powders. Therefore, the possibilities for new applications are enormous. We assume that more attention will be paid to this method with respect to generating dry nanoparticles for many new applications with the central focus remaining catalyst materials.

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