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The size effect of titania-supported Pt nanoparticles on the electrocatalytic activity towards methanol oxidation reaction primarily via the bifunctional mechanism

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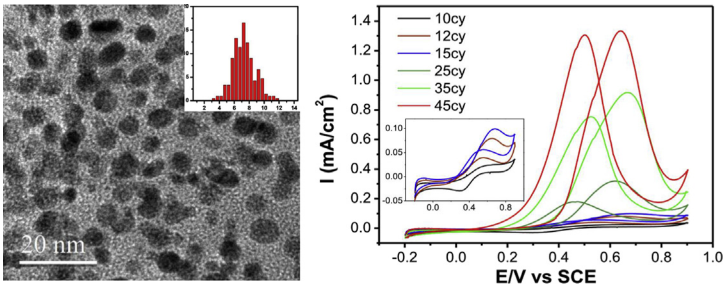
HIGHLIGHTS

- Pt nanoparticles were deposited on native TiO_2 surface by plasma-enhanced ALCVD.
- The effect of Pt particle size on electrocatalytic activity toward MOR was studied.
- Insignificant electronic interaction between Pt particles and TiO_2 was found by XPS.
- Electrocatalytic enhancement for nanoparticles is mainly via bifunctional mechanism.
- Reaction steps for CO electro-oxidation based on bifunctional mechanism are proposed.

GRAPHICAL ABSTRACT



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ABSTRACT

We prepared Pt nanoparticles of different particle sizes by plasma enhanced atomic layer deposition (PEALD) on the native oxide surface layer of Ti thin films, and investigated the Pt particle size effect on the electrocatalytic activity towards methanol oxidation reaction (MOR) in acidic media. The average Pt nanoparticles size ranges from 3 nm to 7 nm depending on the number of the PEALD reaction cycles. The electronic interaction between Pt nanoparticles and the TiO_2 support is insignificant according to x-ray photoelectron spectroscopy analyses, suggesting that the influence of the Pt particle size on the electrocatalytic activity can be mainly described by the bifunctional mechanism. From cyclic voltammetry measurements, Pt particles of smaller size have a better CO tolerance in MOR. We proposed the reaction steps for the electrooxidation of CO adspecies on Pt nanoparticles on the basis of the bifunctional mechanism. The electrode with Pt nanoparticles of ~5 nm in size shows the best electrocatalytic performance in terms of CO tolerance and electrochemical stability.

1. Introduction

Direct methanol fuel cells (DMFCs) using Pt as the catalyst have been widely studied for decades because of their high energy-conversion efficiency, light weight and long operation life under

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ambient conditions. However, the use of precious platinum is always an important concern for the commercialization of DMFCs. Therefore, to reduce the Pt loading without sacrificing the electrochemical performance is a pivotal task for the development of DMFC technology. The approach used most often is the use of dispersed Pt nanoparticles on the catalyst support of large surface area [1–7]. A smaller Pt nanoparticle has a larger electrochemical surface area (ECSA) due to a larger surface to volume ratio and thus shows better utilization of the precious catalyst. Moreover, the smaller size can improve the tolerance towards CO poisoning, which results from incomplete methanol oxidation, via the bifunctional mechanism and the electronic effect [8–13]. The bifunctional mechanism is widely used to describe how oxidation of CO adspecies on Pt sites is enhanced by neighboring hydroxyl surface groups. The electronic effect, which can improve the kinetics of methanol and CO oxidation, is a result of the modification of the electronic structure of Pt sites due to charge transfer with adjacent atoms. To improve the electrocatalytic activity and CO tolerance of a Pt catalyst in methanol oxidation reaction (MOR) by means of the bifunctional mechanism and the electronic effect, one can alloy Pt with other metals, such as Ru, Ni, Mo, Cu, Co and Ag [14–20], or load the Pt catalyst on a transition metal oxide support, such as TiO_2, ZnO, CeO_2 and PdO [21–28]. Transition metal oxides are generally hydrophilic in nature; the surface of the oxides is rich in hydroxyl adspecies, which can improve the oxidation kinetics of residual CO-adspecies on the Pt catalyst via the bifunctional mechanism. Moreover, the strong-metal-support-interaction (SMSI) between the Pt catalyst and the metal oxide may modify the electronic structure of the Pt catalyst [29,30]. The SMSI effect is much more profound when the Pt catalyst size is on the nanometer scale. A strong SMSI may weaken the CO adsorption strength on the Pt catalyst and thus facilitate the CO oxidation via the bifunctional mechanism, thereby improving the electrocatalytic activity of the catalyst towards MOR.

In one of our previous studies, Pt nanoparticles pulse-electrodeposited on porous TiO_2 thin films exhibited a better electrocatalytic activity towards MOR compared with smooth Pt thin films [23]. We ascribed the improvement in the electrocatalytic performance to the synergism of the bifunctional mechanism and the electronic effect occurring between Pt nanoparticles and the TiO_2 substrate. Because both effects are strongly influenced by the size of Pt nanoparticles, it is difficult to separate individual contributions of the two effects to the enhancement of the electrocatalytic activity of Pt nanoparticles. In this work, we deposited Pt nanoparticles by plasma-enhanced atomic layer chemical vapor deposition (PEALD) on the native TiO_2 surface layer of Ti thin films. The PEALD-deposited Pt nanoparticles exhibit weak electronic interactions with the native TiO_2 surface layer. Therefore, the dependence of the electrocatalytic performance of Pt nanoparticles on the particle size can be understood primarily by the bifunctional mechanism. Moreover, the self-limited growth kinetics of PEALD allows us to properly control the Pt nanoparticle size. PEALD is a promising deposition technique for ultrathin film and nanoparticle growth with advantages of fast deposition rate, low deposition temperature and allowing for *in situ* plasma treatment of the sample surface [31,32]. The thin film thickness or nanoparticle size can be precisely controlled by means of the layer-by-layer deposition approach, which is based on the self-limited growth kinetics of the cycle-by-cycle reaction processes [33–36]. In this work, we adjusted the number of the PEALD reaction cycles to deposit Pt nanoparticles of different particle sizes on the native TiO_2 surface, and studied the influence of the particle size on the electrocatalytic properties of the PEALD-Pt nanoparticles towards MOR.

2. Experimental

2.1. Preparation of the Pt/TiO_2 catalyst and material characterization

Pt nanoparticles were deposited at 200 °C on the native TiO_2 surface layer grown on a Ti thin film deposited on a Si(100) wafer. The PEALD Pt precursor was trimethyl-methylcyclopentadienyl-platinum and Ar was the carrier gas. Each PEALD reaction cycle consisted of four steps. First, the TiO_2 substrate was exposed to a Pt precursor pulse of 6 s with the Ar carrier gas flow of 30 sccm, followed by an Ar purge of 100 sccm for 10 s. The oxygen plasma was then ignited at an RF power of 5 W with the O_2 flow rate of 50 sccm for 0.5 s. The PEALD reaction cycle was completed by a final Ar purge for 10 s to remove residual weakly bound adspecies. The size of Pt nanoparticles was controlled by varying the number of the PEALD reaction cycles. For the fabrication of the TiO_2 support, a 100 nm-thick Ti thin film was first deposited on the Si(100) wafer by electron beam evaporation deposition. According to x-ray photoelectron spectroscopy analysis (XPS), a native TiO_2 surface layer with a thickness larger than 5 nm can be grown on the Ti thin film after storage in ambient air for 24 h.

Chemical states of Pt and Ti on the sample were studied by x-ray photoelectron spectroscopy (XPS, Thermo VG 350) using a Mg K_α x-ray source. A gold dot was deposited on the sample by electron beam evaporation for binding energy calibration. The particle size distribution of Pt nanoparticles was analyzed by transmission electron microscopy (TEM, JEOL JEM-3000F). The TEM specimens were prepared by mechanically scratching the Pt/TiO_2 layer off the Si substrate.

2.2. Electrochemical measurements

Cyclic voltammetry (CV) measurements were carried out in a three-compartment cell with a Pt plate as a counter electrode and a saturated calomel electrode (SCE) as the reference electrode. All aqueous solutions were prepared using deionized water of high resistance (~18 MΩ). The electrolyte for the MOR CV measurement, which was carried out in the potential range between −0.2 and 0.9 V vs SCE, was a solution of 0.5 M H_2SO_4 and 1 M methanol. Before the CV measurement, the electrolyte was purged with N_2 for 10 min to remove dissolved gases. The CO stripping measurement was performed in the 0.5 M H_2SO_4 solution in the same potential range as the MOR CV measurement. Adsorption of CO on the Pt catalyst was conducted by flowing a gas mixture of 10% CO/N_2 into the electrolyte at 0.1 V for 40 min, followed by a N_2 purge for 10 min to remove residual CO in the solution. The ECSA was determined in terms of the anodic oxidation peak in the CO stripping CV. The mass loading of Pt nanoparticles, which is needed for the ECSA measurement, was analyzed by inductively coupled plasma mass spectrometry (ICP-MS, Perkin Elmer SCIEX ELAN 5000).

3. Results and discussion

Fig. 1(a) and (b) show bright field TEM images of Pt nanoparticles deposited on the native TiO_2 surface layer with 12 and 50 PEALD reaction cycles, respectively. Fig. 1(c) presents a high resolution TEM (HRTEM) image of Pt nanoparticles deposited with 40 PEALD cycles, in which the lattice fringes marked by red (in the web version) lines corresponds to the Pt (111) plane. It is difficult to estimate the density of Pt nanoparticles on the TiO_2 surface layer from the TEM image because the integrity of the Pt nanoparticles/TiO_2 structure was destroyed by the TEM specimen preparation. However, the TEM images in Fig. 1(a) and (b) clearly demonstrate that the nanoparticle density increases with the number of the