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Atomic force microscopy of cubic Pt nanoparticles in electrochemical environments

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ABSTRACT

Real structure of cubic Pt nanoparticle has been studied at various potentials in 0.1 M $NaClO_4$ with the use of atomic force microscopy (AFM). Cubic Pt nanoparticles in 10 nm height are clearly imaged from 0.10 V to 1.10 V (Ag/AgCl). The height of the nanoparticle increases 1.2 ± 0.7 nm (10.4 ± 6.8%) around the onset potential of oxygen evolution (1.20 V (Ag/AgCl)). The height increase is attributed to the formation of the oxide species at the inner layers of the nanoparticle. Dissolution of the nanoparticle starts from the upper terrace, not from the edge above 1.40 V (Ag/AgCl).

1. Introduction

Pt nanoparticles are used as electro-catalysts of fuel cells. Reduction of the Pt loading in the electro-catalysts is one of the most important subjects for the development of fuel cells because of the small amount of Pt resources. Enhancement of the catalytic activity for oxygen reduction reaction (ORR) and the durability of the electro-catalysts will promote the reduction of the Pt loading. Studies on Pt single crystal electrodes show that the activity for ORR depends on the surface structure strongly: Pt(1 0 0) < Pt(1 1 1) < Pt(1 1 0) [1,2]. Formation of the oxide film induces the dissolution of Pt [3]. The onset potential of the oxide film formation also depends on the surface structure, increasing positively as Pt(1 1 0) < Pt(1 0 0) < Pt(1 1 1) [4]. If we can fabricate the surface structure with high activity and durability on Pt nanoparticles, the Pt loading will be reduced extremely. Shape-controlled Pt nanoparticles play a key role for this strategy. Fig. 1a shows a hard sphere model of a cubic Pt nanoparticle. Planes and edges of the nanoparticle consist of (1 0 0) and (1 1 0) structure, respectively.

Shape-controlled Pt nanoparticles, such as cubic and tetrahedral shapes, have been prepared using polymers as capping reagents [5–11]. Electrochemical deposition and polishing methods provide polyhedral nanoparticles [12]. Catalytic activity of a nanoparticle depends on the shape and the size [13–17]: cubic Pt nanoparticles exhibit higher catalytic activity for ORR than polycrystalline nanoparticles [13,15].

Elucidation of the dissolution mechanism of shape-controlled Pt nanoparticles is important for the development of the electro-catalysts with high durability. *In situ* measurements of the real structures of nanoparticles are necessary for this purpose. Transmission electron microscopy (TEM) is widely used for the observation of the real structures of Pt nanoparticles. However, TEM cannot image nanoparticles in electrochemical environments because high vacuum is necessary for the measurement. Atomic force microscopy (AFM) is one of the powerful methods for the *in situ* measurement of nanoparticles. In this communication, we have measured the real structure of cubic Pt nanoparticles in electrochemical environments. Potential dependence of the shape and the dissolution mechanism are discussed.

2. Experimental

Cubic Pt nanoparticles were prepared according to the previous reports [6,11,16]. The solution of 1 mM K_2PtCl_4 was aged at 40 °C for 10 h. The solution of 1 mM sodium polyacrylate (PAA: averaged molecular weight of 30,000–40,000) was added to 50 ml of the K_2PtCl_4 solution to adjust the each concentration of Pt, PAA and NaI to 1 mM in a vessel. Adsorbed iodine from NaI also works as a capping reagent to provide cubic shape [11]. The pH of the solution was adjusted to 8.8 by the addition of diluted NaOH solution. Ar (purity: 99.9999%) was bubbled through the solution for 30 min, and then H_2 (purity: 99.9%) was bubbled for 10 min at 100 ml min^{-1} to reduce $PtCl_4^{2-}$ to Pt. The vessel was strictly sealed,

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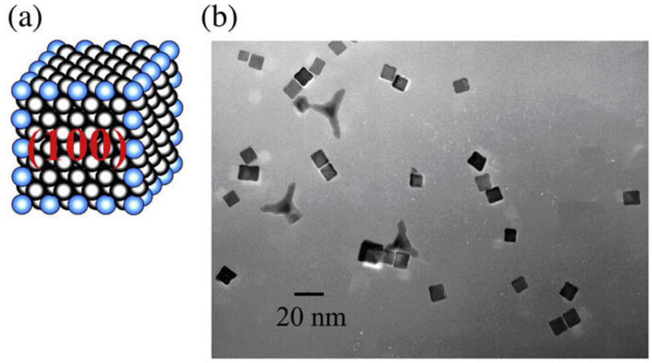

Fig. 1. (a) Hard sphere model of a cubic Pt nanoparticle and (b) TEM image of the prepared cubic Pt nanoparticles.

and left at 40 °C for 10 h under H_2 atmosphere without stirring. The nanoparticles were supported on a substrate without further purification.

Prepared Pt nanoparticles were observed with TEM (JOEL, JEM-4000). The shape and the size distributions of the nanoparticles were determined by counting more than 250 particles in the TEM images.

AFM was measured using PicoSPM 4500 (Agilent Technology) with Magnetic AC mode. Slow dissolution of the nanoparticles is expected in neutral solutions; we adopted 0.1 M $NaClO_4$ saturated with air as electrolytic solution. $NaClO_4$ has no anion that is strongly adsorbed on Pt nanoparticles. The tip radius of the cantilever was about 10 nm. Cubic Pt nanoparticles were supported on a mechanically polished Pt plate. Counter electrode (Pt wire) and reference electrode (saturated Ag/AgCl) were set in an originally designed electrochemical AFM cell.

K_2PtCl_4, PAA and NaI (reagent grade) were purchased from Wako Pure Chemicals. $NaClO_4 \cdot xH_2O$ (purity: 99.99%) was obtained from Aldrich. All the solutions were prepared from ultrapure water treated with Milli Q Advanced (Millipore).

3. Results and discussion

Fig. 1b shows TEM image of prepared cubic Pt nanoparticles. The ratio of cubic nanoparticles is 56.3% in all the particles in the TEM image. The averaged size of the cubic nanoparticles is 9.44 nm. Fig. 2 depicts voltammogram of cubic Pt nanoparticles supported on a Pt plate in 0.1 M $NaClO_4$ saturated with air. Coverage of the Pt nanoparticles must be adjusted as low as possible for the observation of high resolution AFM image of the nanoparticles; the voltammogram is similar to that of a polycrystalline Pt electrode without nanoparticles.

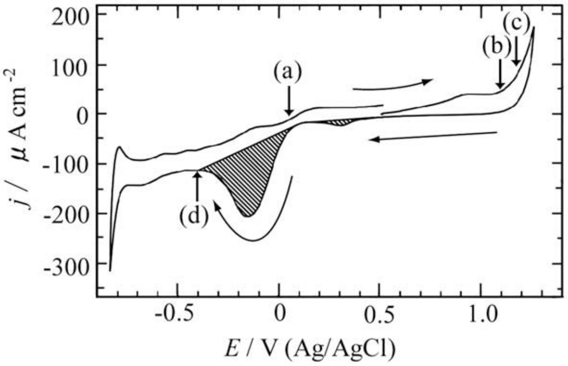

Fig. 2. Voltammogram of Pt nanoparticles on a Pt plate in 0.1 M $NaClO_4$ saturated with air. The shadowed area shows the reduction peak of the oxide film.

Fig. 3 shows *in situ* AFM images of cubic Pt nanoparticles at 0.10 V (Ag/AgCl) in 0.1 M $NaClO_4$ saturated with air. Square shape of the nanoparticle is clearly imaged. The height of the nanoparticle is about 10 nm. However, the width (30 nm) is larger than that of the TEM image. This contradiction is due to the tip convolution effect [18]. The lateral AFM image is the sum of the width of the particle and the tip diameter. The width of the nanoparticle becomes about 10 nm after the correction of the tip diameter (about 20 nm), agreeing with that obtained from the TEM image.

Fig. 4 shows the potential dependence of AFM image of a cubic Pt nanoparticle. The nanoparticle keeps the height and the width between 0.05 and 1.10 V (Ag/AgCl). At the onset potential of oxygen evolution reaction (1.20 V (Ag/AgCl)), the height of the nanoparticle increases 1.2 ± 0.7 nm (10.4 ± 6.8%). The height decreases at 1.40 V (Ag/AgCl), whereas the width does not change. This fact indicates that the dissolution of cubic Pt nanoparticle starts from the upper terrace, not from the edge. Dissolution from the edge is found above 1.50 V (Ag/AgCl). The shape of the nanoparticle becomes disordered above this potential. Although only one nanoparticle is shown in Fig. 4, the height increase and the dissolution from the upper terrace are reproducible. The nanoparticle may be covered by the capping reagents (PAA and iodine) at lower potentials. Adsorbed iodine is oxidized at 0.44 V (Ag/AgCl) on Pt(1 1 1) according to the previous report [19]. Our other AFM measurements show that PAA is oxidized above 1.0 V (Ag/AgCl). We measured voltammogram of cubic Pt nanoparticles on Au substrate to confirm the removal of adsorbed iodine. However, the voltammogram gave small peak of adsorbed hydrogen even after holding the potential at 1.0 V (Ag/AgCl). This result indicates that adsorbed iodine is adsorbed on the Pt nanoparticles more strongly than the bulk Pt electrodes.

It is noteworthy that the height of the nanoparticle increases at the onset potential of the oxygen evolution. There are two possible mechanisms of the height increase: (1) the oxide formation proceeds to the inner layers of the nanoparticle, (2) Pt dissolved from the substrate is re-deposited on the upper terrace of the nanoparticle. The possibility (2) can be neglected, because Pt will not be deposited on the nanoparticle at the dissolution potential of Pt. In addition, the height increase was also found when cubic Pt

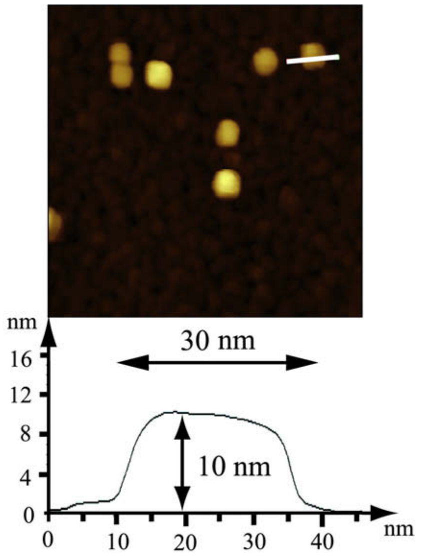

Fig. 3. AFM image of cubic Pt nanoparticles on a Pt plate at 0.10 V (Ag/AgCl) in 0.1 M $NaClO_4$ saturated with air.