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Effect of electron irradiation on nanogroove-networked single-crystalline and dendritic polycrystalline platinum nanosheets prepared from lyotropic surfactant liquid-crystal templates

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Abstract

Using transmission electron microscopy (TEM) electron irradiation effects were studied for nanogroove-network structured single-crystalline and dendritic polycrystalline Pt nanosheets 50–60 nm in size. These two nanosheets with nearly the same average groove-width or dendritic spacing of 1.3–1.4 nm were prepared from the mixed and single surfactant liquid crystalline templates, respectively. On exposure to electron beam for 20 min at the acceleration voltage of 200 kV, the nanogrooved nanosheets were morphologically little affected, but the dendritic ones were transformed into less branched polycrystalline structures with spacings distributed around \sim 1.7 nm. The shape transformation of the latter occurred by the combined mechanism of segmental migration and atomic diffusion. These observations indicate that the nanogrooved Pt nanosheets are highly stabilized by the grooved but crystallographically continuous Pt framework, leading to their extremely high thermo-resistance, in marked contrast to the polycrystalline dendritic structures constructed of crystallographically discontinuous linkages of nanoblocks. © 2007 Elsevier Ltd. All rights reserved.

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1. Introduction

Nanoscale platinum particles have attracted particular attention because of their potential use as catalysts in various fields such as petroleum chemical processes, depoisoning of exhaust gas from automobiles, and polymer electrolyte fuel cells [1]. The catalytic activity of Pt used for these applications depends on the size and the shape of the nanoparticles including the arrangement of surface atoms [2]. Various methods have been therefore developed for controlling the size and the shape of Pt nanoparticles [3], and fabricating unconventional Pt nanostructures including nanorods [4], nanotubes [5], and 2D and 3D mesoporous solids [6,7]. Except for a controlled polyol process [8], most

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of these nanostructured Pt materials were prepared by templating approaches using 2D mesoporous silica or alumina [4], silver wires [5], 3D mesoporous silica [6], and surfactant molecular assemblies [7]. Many catalytic reactions occur at elevated temperatures and even in polymer electrolyte fuel cells operated at relatively low temperatures the catalysts undergo grain growth due to migration of small particles [9]. Not only high catalytic activity but also high thermal stability free from interparticle aggregation would be therefore desired for Pt nanopartcles as catalysts. El-Sayed et al. observed the shape transformation of cubic and tetrahedral Pt nanocrystals with about 8 nm in diameter on a carbon grid under transmission microscope [10]. The particle shapes showed no change at temperatures up to \sim 350 °C, but a small truncation developed at temperatures between 350-450 °C until the Pt nanocrsytals underwent explicitly the shape transformation at about 600 $^{\circ}$ C much lower than the melting point of bulk Pt (1769 $^{\circ}$ C), leading to the shape change and the coalescence of the surfaces of neighboring nanocrystals. Silver nanoparticles of triangle in shape with the curvature of about 5 nm on mica exhibited the shape transformation at room temperature far lower than that of the bulk [11]. Diffusion as dislocation of Pt clusters on Pt (1 1 1) was also observed for a series of clusters up to pentamers at a temperature as low as 350 K [12]. Many other studies have been reported concerning the diffusion of twodimensional islands or large clusters on surfaces [13–24]. Electron microscopy was effectively used to observe the shape transformation or qusimelting of metal nanoparticles under electron irradiation [18–24]. On the other hand, our recent study demonstrated the synthesis of Pt nanotubes by the reduction of H_2PtCl_6 confined to lyotropic liquid crystals (LCs) of polyoxyethlene-type mixed surfactants of polyoxyethylene (20) sorbitan monosteare (Tween 60) and nonaethylene-glycol ($C_{12}EO_9$) [25]. Furthermore, the reduction of Pt salts confined to the hemicylindricl micelles of the same polyoxyethlene-type single or mixed surfactants on graphite yielded Pt nanosheets with a uniform thickness of as thin as 3.5 nm [26] and in situ atomic force microscopy (AFM) also revealed that the Pt nanosheets undergo the shape transformation and the coalescence in preferred directions at room temperature [27]. More recently, nanogroove-network structured single-crystalline nanosheets \sim 3.5 nm thick were synthesized by the reduction of Na_2PtCl_6 with $NaBH_4$ using the same mixed surfactant LC templates, although a similar reaction using the Tween 60 based single surfactant LC templates yielded morphologically similar but 2D dendritic polycrystalline Pt nanosheets [28]. We also found that the nanogrooved Pt nanostructures loaded on carbon exhibit fairly high electrocatalytic activity for oxygen reduction reaction [28]. It would be thus of importance to characterize the structural stability of these functionally unique Pt nanostructures obtained in the surfactant templating systems. Here we report the extremely high resistance of nanogroove-network structured single-crystalline nanosheets to electron irradiation, in marked contrast to 2D-dendritic polycrystalline nanosheets showing the shape transformation into 2D less branched polycrystalline ones by the combined mechanism of segmental migration and atomic diffusion within the individual nanosheets.

2. Experimental

2.1. Materials

Hydrogen hexachloroplatinate(IV) hexahydrate ($H_2PtCl_6 \cdot 6H_2O$) was purchased from Wako Chemical Co. and it was neutralized with NaOH or LiOH into sodium or lithium hexachloroplatinate (Na_2PtCl_6 or Li_2PtCl_6) prior to use. Nonaethylene-glycol monododecyl ether ($C_{12}EO_9$) and Polyoxyethylene (20) sorbitan monostearate (Tween 60) were purchased from Wako Chemical Co. and used without further purification. Other chemicals were of reagent grade. Sodium borohydride (NaBH₄; SBH) was also used as received from Wako Chemical Co. The chemical structure of Tween 60 is shown in Fig. 1.

2.2. Synthesis

In the typical reaction, Na₂PtCl₆ (7.54 × 10⁻⁴ mol), $C_{12}EO_9$ (7.54 × 10⁻⁴ mol), Tween 60 (7.54 × 10⁻⁴ mol), and H₂O (4.52 × 10⁻² mol) at a 1:1:1:60 molar ratio were mixed in a glass tube of 15 mm in inner diameter at 60 °C for 15 min, and then cooled to 20 °C and allowed to stand at that temperature for 30 min. SBH (7.54 × 10⁻⁴ mol) was dissolved in water (15.1 × 10⁻³ mol) and then added to the precursory pasty mixture to keep at that temperature for 24 h. After the reaction mixture being mixed with water, the resulting solid was separated from the solution containing unreacted Na₂PtCl₆ species, washed with water and then with ethanol prior to drying in air. Similar reactions using Li₂PtCl₆ instead of Na₂PtCl₆ and Tween 60 alone instead of C₁₂EO₉ and Tween 60 were carried out as above.



Fig. 1. Chemical structure of Tween 60.

2.3. Characterization

All TEM and HRTEM images were taken with a JEOL-2010 microscope operated at 200keV. Small-angle XRD patterns for pasty samples were measured by the transmission method using Cu K α radiation on a Shimadzu XRD-7000 diffractometer equipped with a glass plate of 1 mm thick with a slit of 1 mm wide filled with specimen.

2.4. Electron irradiation

The experiments were carried out as follows: The sample for investigation was placed on a micro-grid (Nisshin EM Co., 200 mesh) after ultrasonication in ethanol. First, a high resolution TEM image of the area selected for the subsequent irradiation was taken to characterize the original morphology of sample. Then the sample was irradiated for a prescribed time up to 20 min with an electron beam generated using the acceleration voltage of 200 kV while the TEM image of the same area was taken at 5-min intervals.

3. Results and discussion

The resulting products in the Tween 60 based mixed surfactant systems were identified as single-crystalline nanosheets of ~50 nm in size with a nanogroove-network as described elsewhere [28], according to their transmission electron microscope (TEM) images (Fig. 2a and b): The continuous atomic fringes with a spacing of 0.23 nm observed over 20 nm or above confirmed that the elliptic nanoleaves ~2.5 nm wide and 2–4 nm long are connected with their crystallographic alignment to form a single-crystalline nanosheet with a nanogroove-network (Fig. 2b). Based on the TEM image, the single-crystalline nanosheets were characterized by the presence of nanogrooves with a narrow distribution of groove-widths centered at ~1.4 nm (Fig. 2a). Similar nanogroove-network structured single-crystalline nanosheets were obtained by the reaction using Li₂PtCl₆ instead of Na₂PtCl₆ (Fig. 2f). This product showed the development of nangrooves of as wide as ~1.2 nm with a narrow distribution of groove-widths. On the other hand, the resulting products in the Tween 60 based single surfactant systems were identified as 2D dendritic polycrystalline nanosheets of ~ 60 nm in size (Fig. 3a–c). The dendritic nanosheets gave an average spacing of ~1.3 nm but with a broad distribution ranging from 0.8 to 2.4 nm. The crystallographic difference between the single-crystalline and the polycrystalline nanosheets was also confirmed by their Fourier transform patterns (inset) indicative of a pair of spots and four or more pairs of spots, respectively.

Solidification from a melt commonly occurs as directional growth of dendritic arrays and a typical freely grown dendrite forms straightly developed primary stem and sidebranches [29]. In contrast, as seen from the TEM images, the present nanogrooved and the dendritic nanosheets are formed of meandered branches because the nanosheets were grown in a LC medium in which the path for platinate and reductant species to diffuse is spatially restricted and complicated. It is also remarked that the nanogrooved nanosheets exhibit a narrow distribution of groove-widths, whereas the dendritic nanosheets show not only a dendritic branching pattern (Fig. 3c) but also a wide distribution of spacings characteristic of dendritic growth [29,30]. This fact suggests that the grooved nanosheets would grow by a mechanism essentially different from that expected for the other ones. The striking difference between the structural properties and growth patterns of the nanosheets produced in the Tween 60 based mixed and single surfactant systems would be arisen from that between their precursory liquid crystalline phases identified as hexagonal and lamellar LCs,



Fig. 2. TEM or HRTEM images of the Pt nanoparticles (a and b) as grown and (c–e) electron irradiated in the lyotropic mixed surfactant Na₂PtCl₆/ $C_{12}EO_9$ /Tween 60 system and (f) as grown Pt nanoparticles in the lyotropic mixed surfactant Li₂PtCl₆/ $C_{12}EO_9$ /Tween 60 system, together with distributions of groove-widths: irradiation time, (a, b, f) 0 min, (c) 10 min and (e) 15 min. The HRTEM image of the box area in (a) is given in (b). The Fourier transform patterns taken at the initial and final stages of electron irradiation are given in inlets, showing two spots indicating that the sheet is single crystalline.

respectively [27,28]. In the 2D-hexagonal array of cylindrical micelles for the former the chemical species or reduced Pt clusters can move much more easily along the micellar axis than in a direction perpendicular to it, as observed in a 2D array of heimicylindrical micelles of Tween 60 [26]. This might be more favorable for the partial coalescence of Pt nanoleaves with their crystallographic alignment. In the lamellar LCs of Tween 60 bimolecular layered micelles for the other nanosheets the doped materials can move freely in the 2D-isotropic space, but reductant species are supplied only through the edge of the lamellar LCs, resulting in the growth of crystallographically discontinuous dendrites. The nanogroove-network structured single-crystalline nanosheets produced in the Na-platinate system showed a little smaller groove-widths than those in the Li-platinate system. This might be also resulted from the structural difference between their precursory LCs. Fig. 4 shows the XRD patterns of the M₂PtCl₆/C₁₂EO₉/Tween 60/H₂O mixtures at a x:1:1:60 molar ratio for the M = Li and M = Na systems. The major peak and a very weak band near $2\theta = 2.5^{\circ}$ for both mixtures can be attributed to the 100 and 110 reflections for a hexagonal structure with a = 7-7.4 nm. The peak intensities of 100 reflection for the Li- and Na-platinate mixtures showed a more marked tendency to decrease with an increase of x in that order. In accord with these tendencies, the parameter a of 7.4 nm for the precursory Li-platinate LC phase at x = 1 was larger than 7.3 nm for the Na–platinate phase, probably because the cylindrical micelles in the former phase containing hydrated Li ions is more expanded than those in the latter containing hydrated Na ions with a smaller radius. The more expanded space formed by the 2D-hexagonally array of wider cylindrical micelles for the Li-platinate system might lead to an increase in groove-width.

On electron irradiation for 5 min or more up to 20 min using the acceleration voltage of 200 kV the nanogroovenetwork structured single-crystalline Pt nansheets prepared in the Na–platinate system showed no changes in morphology, as confirmed by the groove-width distributions independent of irradiation time (Fig. 2a and c–f, Fig. 5).



Fig. 3. TEM or HRTEM images of the Pt nanoparticles (a and b) as grown and (d–g) electron irradiated in the lyotropic Tween 60 based single surfactant $Na_2PtCl_6/Tween 60$ system, together with their distributions of spacings: irradiation time, (a and b) 0 min, (d) 5 min, (e) 10 min, (f) 15 min, and (g) 20 min. The HRTEM image of the box area in (a) is given in (b). The Fourier transform patterns taken at the initial and final stages of electron irradiation are given in inlets. The branched framework of a dendritic nanosheet in (a) is illustrated in (c).

No structural change by electron irradiation was also observed for the nanogroove-network structured nanosheets obtained in the Li-platinate system. In marked contrast, on exposure to electron beam for 5-20 min the 2D dendritic polycrystalline nanosheets prepared in the Tween 60 based single surfactant system were gradually coalesced into less branched dendritic polycrystalline nanosheets: the spacings of the dendritic nanosheets and their distribution were appreciably increased from ~ 1.3 nm and 0.8-2.4 nm at irradiation time t = 0 min into ~ 1.7 and 1-2.6 nm at t = 20 min, respectively, with an accompanying enrichment of closed spaces (Figs 3 and 5). Fig. 6 shows the morphological change before and after irradiation as well as the detailed coalescence process of Pt nanoleaves or islands 3-4 nm wide and 4-5 nm long with crystallographically different orientations in a selected area of the same dendritic nanosheet sample. In this process, the left part of nanoleaf B is separated from the right part to move to nanoleaf A, leading to their coalescence at irradiation time $t = 10 \min$ (Fig. 6e): at $t = 5 \min$ the nanoleaf B is just about to be separated into two parts (Fig. 6d). Moreover, the coalescence is accompanied by the atomic rearrangement so that the Pt atoms at the outer part of A are diffused to occupy the empty space located around the center of the selected area. The round space remained unoccupied was fully occupied with Pt atoms at t = 35 min, resulting in a single-crystalline leaf with a size of 6–8 nm (Fig. 6h). It is known that the grain growth of Pt clusters or nanoparticles with different sizes proceeds by Ostwald ripening based on the diffusion of atoms from small to large particles [31] or by the migration of small particles to coalesce with larger ones [32,33]. The shape transformation of the present 2D dendritic Pt nanosheets by electron irradiation could be therefore explained by the combined mechanism of the small leaflet migration and the atomic diffusion based on Ostwald ripening, as schematically shown in Fig. 7B. The model



Fig. 4. XRD patterns of the (A) Li₂PtCl₆/C₁₂EO₉/Tween 60/H₂O and (B) Na₂PtCl₆/C₁₂EO₉/Tween 60/H₂O mixtures at a molar ratio of *x*:1:1:60 for x = 0, 0.2, 0.4, 0.6, 0.8. and 1.0 (Cu K α). (C) Plots of lattice parameter *a* as a function of platinate amount added for the Li–platinate (squares) and Na–platinate (circles) LC phases.

(C) in Fig. 7 illustrates a decrease of the number of branches and broadening of dendritic spacings resulted from the structural change of the nanosheets upon electron irradiation. Since the dendritic polycrystalline Pt nanosheets are an aggregate of Pt nanoparticles with high edge surface and interfacial energies [27], the energy supplied by electron irradiation would induce the movement of Pt nanoleaves (or islands) or atoms so as to minimize the total surface energy of the Pt aggregate. The nanometer- or atomic-scale movement may be caused by the atomistic processes such as evaporation–recondensation of single atoms between the islands and a surrounding two dimensional gas [17], edge running of atoms around the island perimeter [34] or some other mechanism, although the detailed shape transformation mechanism of the Pt nanosheets are not obvious at the present stage. On the other hand, the nanogrooved single-crystalline Pt nanosheets are free from interfacial energy in comparison with the dendritic nanosheets even if both structures are similar in shape (Fig. 7A), which would raise the thermodynamic stabilities of the former nanosheets leading to their high resistance to electron irradiation for as long as 20 min.



Fig. 5. Plots of average groove-width and dendritic spacing as a function of irradiation time for the nanogroove-networked single-crystalline (\Box) and dendritic polycristalline (\bigcirc) nanosheets.



Fig. 6. Sequence of TEM images showing a selected area (circle) of a dendritic Pt nanosheet changing from an initial phase to the shape transformed phase during electron irradiation: Irradiation time, (a and c) 0 min, (d) 5 min, (e) 10 min, (f) 20 min, (g) 30 min, and (b and h) 35 min.



Fig. 7. A schematic illustration of the shape transformation of (A) nanogrooved single-crystalline and (B and C) dendritic polycrystalline nanosheets during electron irradiation.

Under irradiation of electron beam at an energy of 200 keV heating occurs predominantly through ionization processes and radiation losses may be ignored [35]. It is therefore believed that the Pt nanoparticles exposed to electron beam underwent the explicit shape transformation by the heating effect of the beam. Thus, the above observations clearly indicate that the nanogrooved but single-crystalline Pt nanosheets are thermally much more resistant than the polycrystalline Pt ones because the former nanostructures are highly stabilized by the grooved but crystallographically continuous Pt framework, in marked contrast to the polycrystalline branched structures constructed of crystallographically discontinuous linkages of nanoblocks.

4. Conclusions

We demonstrated that nanogroove-network structured single-crystalline Pt nanosheets are morphologically little affected even by 20-min electron irradiation, whereas dendritic polycrystalline nanosheets exposed to electron beam are transformed in shape into less branched polycrystalline ones. The shape transformation of the latter nanosheets proceeds by the combined mechanism of segmental migration and atomic diffusion within the individual nanosheets to minimize their surface and interfacial energies. The striking difference between the resistances of the nanogroove-networked single-crystalline and dendritic polycrystalline Pt nanosheets to electron beam are attributed to whether these two nanostructures are energetically stabilized by their crystallographically continuous Pt framework or destabilized by their crystallographically discontinuous linkages of nanoblocks. Considering the heating effect caused predominantly by electron irradiation, the present results reveal that the nanogroove-network structured single-crystalline Pt nanosheets have extremely high thermo-resistance and hence promising as catalysts for fuel cells and other applications.

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