Three-Dimensional Interstitial Nanovoid of Nanoparticulate Pt Film Electroplated from Reverse Micelle Solution

Sejin Park,† Sun Young Lee,‡,§ Hankil Boo,†
Hyun-Mi Kim,‖ Ki-Bum Kim,‖ Hee Chan Kim,⊥
Youn Joo Song,‡ and Taek Dong Chung*,‡

Nomadien Corporation, 249-1 Dongseon-dong, Sungbuk-gu, Seoul 136-742, Korea, School of Materials Science and Engineering, Seoul National University, Seoul 151-742, Korea, Department of Biomedical Eingineering, Seoul National University, Seoul 110-744, Korea, and School of Chemistry, Seoul National University, Seoul 151-747, Korea

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So far, metal thin films with nanopores on the scale of a few nanometers have been fabricated by electrochemical deposition only in the limited types of surfactant-based templates, such as hexagonal (H_1) lyotropic liquid crystalline (LLC) phase[1] or potential-controlled micelle assembly.[2] Both kinds of templates produce hexagonally ordered (one-dimensional, 1D) nanopores, the mass transport along which could be easily inhibited by pore blocking. In addition to the LLC phase and the micelle-type aggregation, the reverse micelle (L_2) solution is another phase to be potentially exploited as templates for nanostructured materials of higher dimension. However, there rarely has been studies on the nanoporous metal films electroplated from L_2 solution. In this study, we propose a new method to fabricate three-dimensional (3D) nanoporous Pt film via electrochemical deposition in L_2 solution of a nonionic surfactant.

Metallic thin films with nanoporous structure are of great use and importance in the fields of energy storage materials,[3] catalysts,[4,5] and sensors.[6−9] There have been only a few methods introduced to fabricate such nanoporous metal films, for example, electroless plating of Au inside the pores of the membrane filter[10] and dissolution of one component of alloys (dealloying).[11,12] Moreover, to obtain a free-standing nanoporous film with pore size of a few nanometers, the only method has been to electroplate by the aid of templates of self-assembled surfactants, which utilizes either LLC template[1] or potential-controlled surfactant assembly.[2]

Attard et al. reported the electrodeposition of nanoporous Pt (symbolized as H_1-ePt) in the LLC template,[1,13] and the H_1-ePt showed hexagonally arranged pores of approximately 2.5 nm in diameter with a pore−pore distance of approximately 5 nm.[1] Stucky et al.[2] showed that cylindrical/hemicylindrical micelle assembly of surfactant was formed at the electrode/solution interface where electric field was applied and functioned as a template for nanoporous Pt film with pore diameter of approximately 4 nm and wall thickness of approximately 4 nm. Relevant works were also reported for lamellar LLC[14] or LLC of block copolymer.[15]

Although the nanoporous Pt films electroplated from both LLC template and potential-controlled surfactant assembly allow us to take novel advantage of the nanoporous structures in the various applications, there are the issues to be addressed for practical uses; for example, sluggish diffusion along the 1D pore and pore clogging resulting in deactivation of the entire surface of the inner wall. In these respects, the nanoporous structures of higher dimension are expected to alleviate the problems. Although there is a report on 3D nanoporous Pt, it has rarely been fabricated in the form of thin film by electroplating.[16]

In the present study, we propose the L_2 phase as another electroplating environment for nanoporous Pt films. Seemingly the Pt deposition might not readily take place in the L_2 solution, because the aqueous regions containing Pt precursors are individually enclosed by nonpolar moieties of surfactant molecules. However, the proton self-diffusion is reportedly active among the neighboring aqueous domains as the water content exceeds 13 wt % in the L_2 phase of the binary mixture of Triton X-100 and water.[17] Thus it is conceivable that the L_2 phase with relatively high water content may work as an alternative template for electroplating metals. Furthermore, the encounter of micelles and Pt nanoparticles can result in the growth of network of Pt nanoparticles, in the dynamic equilibrium phase of L_2. As Pt nanoparticles grow in the aqueous region of L_2 phase, it is expected that the interstitial voids gradually form the structure of 3D nanopores.

The solution for electroplating Pt in this study was the mixture of Triton X-100 (50 wt %), 0.3 M NaCl aqueous solution (45 wt %), and hexachloroplatinic acid (HCPA; 5 wt %) at 40 °C. The isotropic images from the polarizing

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† Nomadien Corporation.
‡ School of Chemistry, Seoul National University.
§ Present address: Cambridge-ETRI joint R&D centre, ETRI, 161 Gajeong-dong, Yuseong-gu, Daejeon, Korea.
‖ School of Materials Science and Engineering, Seoul National University.
⊥ Department of Biomedical Eingineering, Seoul National University.

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optical microscopy and the electrical conductance unequivocally indicated that the L_2 phase is predominant in the mixture, which is supported by the previous reports[18,19] (see Supporting Information). Pt was electrochemically deposited on a flat Au substrate electrode by applying −0.2 V vs Ag/AgCl at 40 °C, and the Pt film as made was denoted by L_2-ePt. The surface roughness of the L_2-ePt was determined by measuring the area under the hydrogen adsorption peak of the cyclic voltammogram (scan rate, 0.2 V s^{-1}) in 1 M sulfuric acid solution, using a conversion factor of 210 μC cm^{-2}.[20] The morphology of the L_2-ePt was characterized by transmission electron microscopy (TEM) using JEM-3000F (JEOL) with a point-to-point resolution of ~0.17 nm and by field emission scanning electron microscopy (FESEM) using JSM-7401F (JEOL). A L_2-ePt on Si wafer with an adhesive layer of Cr was used to obtain the FESEM and TEM images. Electrochemical experiments were performed with an electrochemical analyzer (model CH660). Ag/AgCl (3 M KCl) and a Pt wire were employed as reference and counter electrodes, respectively (see Supporting Information).

Within several minutes, the current for the electroplating of L_2-ePt reaches a steady state, which means diffusion-controlled reduction of HCPA (see Supporting Information). The steady-state current is substantially large (ca. 3 mA cm^{-2}), which implies that the diffusion of HCPA in L_2 solution is fast enough to keep up the growth rate of the L_2-ePt film.

The FESEM image (Figure 1A) shows very dense and flat surface of the L_2-ePt. The cracks are narrower than 20 nm while no conspicuous grain or pore is observed. The thickness of the L_2-ePt prepared by passing 0.64 C cm^{-2} is ~0.13 μm and remarkably uniform at least throughout the area of 1 cm^2. In contrast with the macroscopic flatness of the L_2-ePt, the TEM images in Figure 1B show obvious nanoporous morphology. The L_2-ePt consists of crystalline (face centered cubic) Pt nanoparticles (~3 nm in diameter) interconnected with others. The interstitial nanopores among the partially merged Pt nanoparticles are quite evenly distributed, and their width is approximately 1−2 nm. The interstitial nanopores of the L_2-ePt have a 3D structure, which notably differs from the 1D nanopores reported in preceding reports.[1,2]

Owing to the the 3D nanoporous structure, the L_2-ePt shows a high roughness factor, for example, 227 when 2.55 C cm^{-2} passed (Figure 2A). Figure 2B shows that the roughness factors of L_2-ePts are proportional to the charge passed during the electroplating (9 × 10 per 1 C cm^{-2}). This indicates that little dead pores are produced as the Pt film grows. Moreover, one can finely control the roughness of L_2-ePt by regulating the charge passed for electroplating.

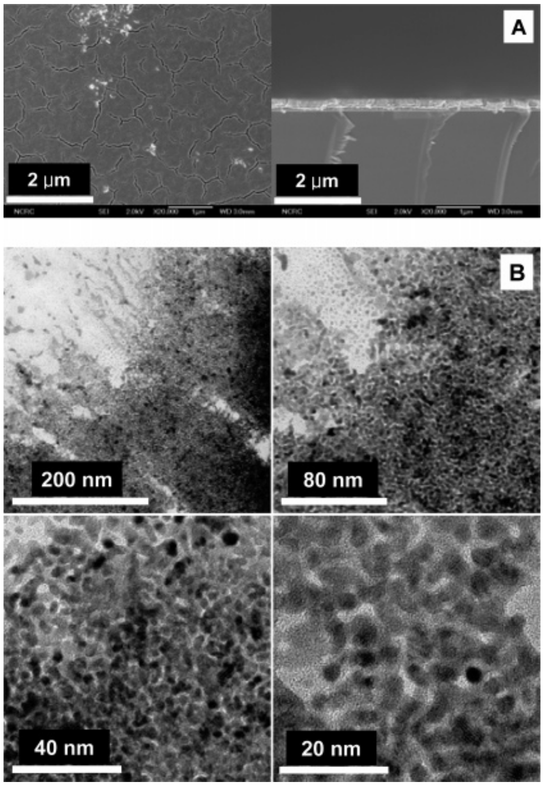

Figure 1. Morphologies of the L_2-ePt electroplated by passing 0.64 C cm^{-2} (A and B): (A) FESEM images observed from the top (left) and side (right), (B) TEM images and HRTEM image (bottom right).

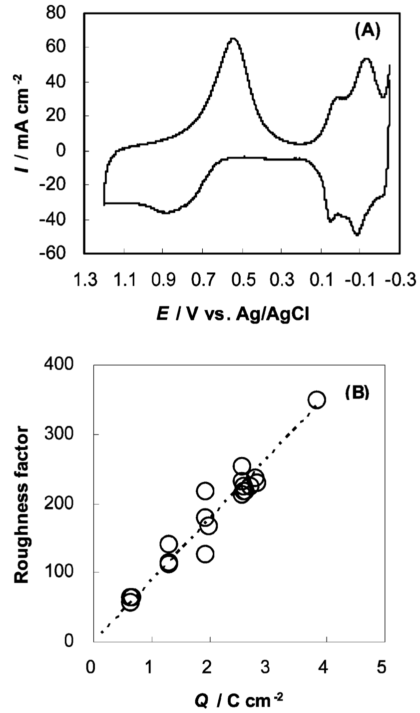

Figure 2. (A) Cyclic voltammogram of a L_2-ePt in 1 M H_2SO_4 (0.2 V s^{-1}) electroplated by passing 2.55 C cm^{-2} and (B) dependence of surface roughness on the charge passed.

According to our previous studies, nanoporous Pt shows unique electrochemical behavior.[8,9,21] H_1-ePt selectively enhances the amperometric signals and thus can be utilized as a nonenzymatic glucose sensor.[9] Moreover, the nanoporosity of H_1-ePt increases the exchange current of the electrode surface and markedly improves the performance as a pH sensing material.[8] The nanoporous Pt fabricated in this study, L_2-ePt, exhibits all of the electrochemical characteristics that H_1-ePt shows. Figure 3A shows the large

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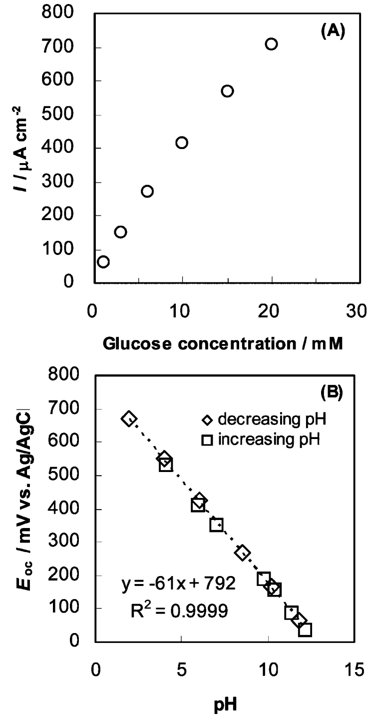

Figure 3. (A) Calibration curve for the glucose responses of L_2-Pt (rf 232) in phosphate-buffered saline (PBS; 0.1 M phosphate, 0.15 M NaCl, pH 7.4) at 25 °C and +0.4 V vs Ag/AgCl. (B) E_{oc} versus pH curves of L_2-ePt in stirred and air-saturated PBS, which was prepared by mixing 0.1 M H_3PO_4 and 0.1 M Na_3PO_4 containing 0.15 M NaCl. E_{oc} was recorded at 60 s after the L_2-ePt was dipped into the solutions. The pH was decreased from 12 to 2 (diamonds) and then elevated to 12 again (squares).

amperometric current from electrochemical oxidation of glucose without the aid of enzyme and the linear responses to 0−20 mM glucose. On the other hand, L_2-ePt gives stable and fast responses to the pH changes, and the plot of open circuit potential (E_{oc}) versus pH in Figure 3B demonstrates perfect Nernstian responses and negligible hysteresis, which strongly suggest the application for a promising solid-state pH-sensing material.

In conclusion, 3D nanoprous Pt film (L_2-ePt) was successfully electroplated from L_2 solution of a widely used nonionic surfactant, Triton X-100. L_2-ePt showed the 3D interstitial pores of 1−2 nm wide and a high roughness factor. By virtue of the 3D porous structure, L_2-ePt is adequate for catalytic applications that require fast mass transport and alleviated pore closing. As an electroplating method for nanoporous films, the results from the present study extend the scope that has been limited within the LLC template or potential controlled self-assembly producing 1D nanopores and suggest a new way toward mass production of nanoporous metal thin films. Also, it will be an interesting issue to control the nanoparticle size and pore width by using other surfactants with various lengths and structures of their chains.

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Supporting Information Available: Discussion of the L_2 phase, experimental details, and current curve during electroplating (PDF). The material is available free of charge via the Internet at http://pubs.acs.org.

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