Fabrication of Ordered Nanostructures in Ta Films Using 2D Array of Ferritin Molecules as Template

Hideki Masuda,*[1,2] Yoshitaka Matsui,[1,2] Tetsuya Miwa,[3] Mitsutaka Nagae,[1] Miyuki Tanji,[1] and Kazuyuki Nishio[1,2]
[1]*Department of Applied Chemistry, Tokyo Metropolitan University, 1-1 Minamiosawa, Hachioji, Tokyo 192-0397*
[2]*Kanagawa Academy of Science and Technology (KAST), 5-4-30 Nishi-hashimoto, Sagamihara 229-1131*
[3]*Japan Agency for Marine-Earth Science and Technology (JAMSTEC), 2-12 Natsusima, Yokosuka 237-0061*

(Received October 27, 2005; CL-051347; E-mail: masuda-hideki@c.metro-u.ac.jp)

Metal (Ta) films with ordered structures of nanometer-scale dimensions were fabricated by replicating the structure of a 2D array of ferritin molecules as a template. The deposition of a Ta layer onto a 2D array of ferritin molecules using ion-beam sputtering and subsequent removal of the ferritin molecules generated Ta films with an ordered array of concave with a 13 nm interval. The uniformity and chemical stability of Ta formed by ion-beam sputtering contributed to the precise replication of the fine structures of the 2D array of ferritin molecules.

Processes for the fabrication of ordered structures of nanometer-scale dimensions have attracted growing interest because of their potential application to the preparation of various types of nanodevices.[1–3] Ordered structures composed of uniform-sized and uniform-shaped biomolecules are possible starting structures for the fabrication of nanodevices.[4] Ferritin molecules, which are composed of spherical protein shells of 13 nm in diameter that have hydrated iron oxide cores, are widely used as the ordered structures for nanofabrication because of their ability to form highly ordered two-dimensional (2D) close-packed arrays.[5–7] Although there have been a few reports on the fabrication of nanometer-sized structure using ferritin molecules as a mask for dry etching, in which the protein shells were in advance eliminated by oxidation,[8,9] there have been no reports of the replication of the ordered 2D structures of ferritin having shells with other materials. In the present work, we report for the first time the fabrication of the ordered structures of a metal (Ta) film by replicating the fine structure of a 2D array of ferritin molecules. The ordered 2D array of ferritin was transferred via the deposition of a uniform thin Ta layer onto the 2D array of ferritin using an ion-beam sputtering technique.

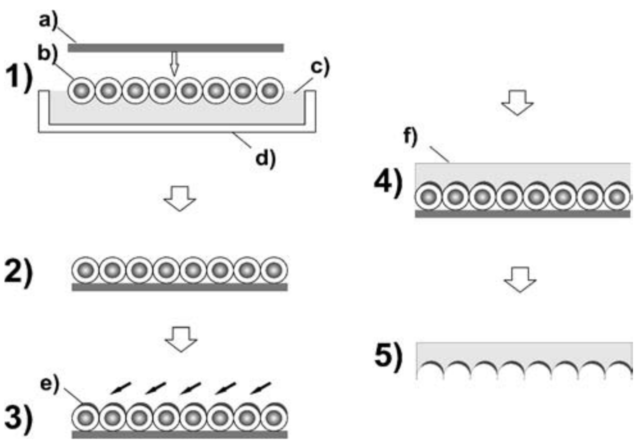

Figure 1. Schematic for fabrication of ordered Ta film from 2D array of ferritin molecules, (1) ordered 2D array of ferritin on solution/air interface, (2) transfer of 2D array of ferritin to Cu microgrid, (3) deposition of Ta layer, (4) reinforcement of Ta by carbon, (5) removal of ferritin molecules and microgrid: (a) Cu microgrid, (b) ferritin, (c) spread solution, (d) PTFE trough, (e) Ta layer, and (f) carbon reinforce layer.

Ferritin (Sigma, 50–70% purity) was purified through gel filtration using a Sephacryl column (Pharmacia S-300HR) in 0.1 M trisbuffer as an extracting solution. The concentration of ferritin was then adjusted to be 3 mg/L in a 0.1 M trisbuffer solution. Figure 1 shows the schematic for the fabrication of the ordered structure of Ta using the 2D array of ferritin as a template. The ordered 2D array of ferritin molecules was obtained via the process reported previously.[5] One microliter of ferritin solution was injected into the solution containing 0.15 M NaCl, 10 mM $CdSO_4$, 10 mM $C_6H_{13}NO_4S \cdot H_2O$, and 2 wt % glucose, the pH of which was adjusted to be between 5.6 and 5.8 using NaOH. After the injection of the ferritin into the spread solution in a PTFE trough ($20 \times 20 \times 2$ mm), the 2D array that was produced on the air/solution interface was transferred to the Cu microgrid (Nissin EM) by slightly touching the grid to the surface of the solution. A Ta layer of 1 nm was deposited onto the 2D array of ferritin by using an ion-beam sputtering apparatus (South Bay Technology) at an angle of 30 degrees to the substrate. Ta was selected for its uniformity and chemical stability in the ion-beam sputtered films. A carbon layer of 10 nm was then deposited onto the Ta layer to reinforce the Ta layer. After the dissolution of the Cu microgrid in the mixture solution of CrO_3 and H_2SO_4, the Ta film was transferred from a rinsing solution to the microgrid. The obtained samples were observed by a transmission electron microscope (TEM: JEOL JEM-1010).

Figure 2 shows TEM images of the 2D array of the ferritin molecules formed on the Cu microgrid. From the low-magnification image in Figure 2a, a highly ordered 2D array of ferritin molecules can be confirmed. From the enlarged image in Figure 2b, ideally arranged ferritin molecules can be observed over the entire field of view. The average interval and size of the iron oxide cores were 13 and 6 nm, respectively. These values are in good agreement with those reported previously.[6] In Figures 2a and 2b, some defect sites of the cores can be observed in the 2D array. These defect sites in TEM images are thought to be the result of the existence of apoferritin in the array, which has no core in it.

Figure 3 shows a TEM image of the Ta film obtained from the 2D array of ferritin molecules as a template. From Figure 3, the existence of an ordered array of concaves throughout the sample can be confirmed. The deposition of Ta at an oblique angle improved the contrast of the TEM images by the shadowing effect. The interval of the concaves was 13 nm, which is in

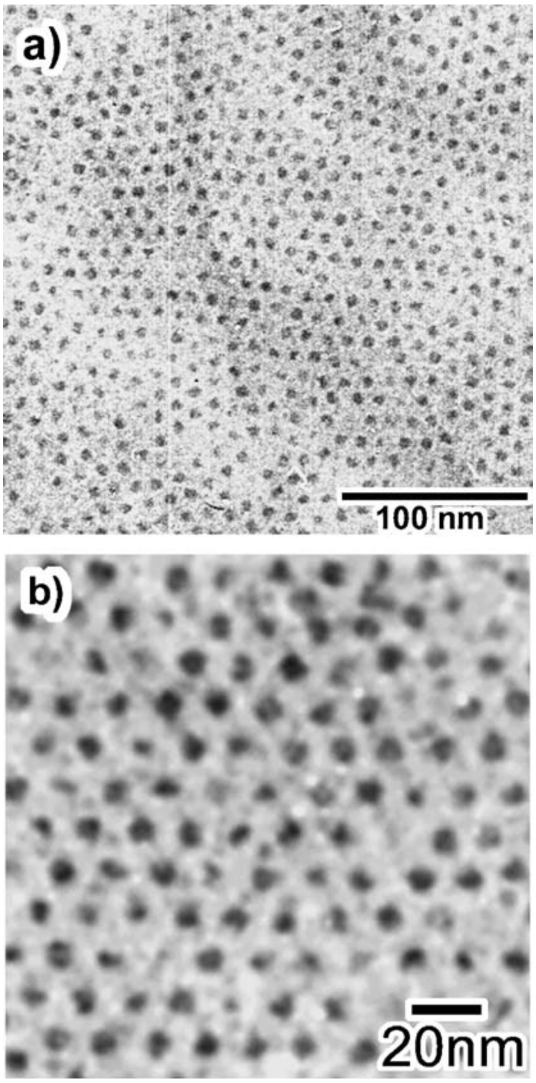

Figure 2. TEM images of 2D array of ferritin; low-magnification (a), and high-magnification (b) images.

good agreement with that of the 2D array of ferritin molecules. From this result, it can be concluded that the 13-nm-period ordered structure of the 2D array of the ferritin molecules was transferred by the ion-beam sputtering of Ta. The ability of ion-beam sputtering to form an extremely uniform thin layer contributed to the precise replication of the nanometer-scale 2D array of ferritin molecules. In addition, the chemical stability of Ta, which was used for the formation the film onto the 2D array of ferritin, also contributed to the precise replication of

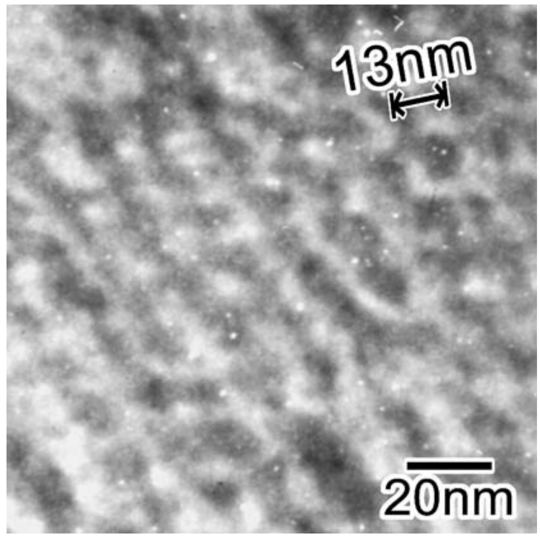

Figure 3. TEM images of ordered structure of Ta film.

the fine structures.

An ordered 2D array of 13-nm-diameter ferritin molecule was successfully transferred to metal (Ta) films using ion-beam sputtering. The surface of the obtained Ta film had a fine and highly ordered structure. With the process described in the present work, unstable ordered structures of biomolecules can be transferred to various kinds of materials, that have sufficient chemical and mechanical stability. Therefore, this technique will be used for the expansion of the application fields of ordered structures composed of various kinds of biomolecules.

References

1 R. J. Tonucci, B. L. Justus, A. J. Campillo, C. E. Ford, *Science* **1992**, *258*, 783.
2 T. M. Whitney, J. S. Jiang, P. C. Searson, C. L. Chien, *Science* **1993**, *261*, 1316.
3 H. Masuda, K. Fukuda, *Science* **1995**, *268*, 1466.
4 K. Douglas, G. Devaud, N. A. Clark, *Science* **1992**, *257*, 642.
5 T. Furuno, H. Sasabe, K. M. Ulmer, *Thin Solid Films* **1989**, *180*, 23.
6 H. Yoshimura, T. Scheybani, W. Baumeister, K. Nagayama, *Langmuir* **1994**, *10*, 3290.
7 T. Miwa, M. Yamaki, H. Yoshimura, S. Ebina, K. Nagayama, *Langmuir* **1995**, *11*, 1711.
8 G. Yamazaki, Y. Uraoka, I. Yamashita, *J. Photopolym. Sci. Technol.* **2003**, *16*, 439.
9 T. Kubota, T. Baba, S. Samukawa, H. Kawashima, Y. Uraoka, T. Furuki, I. Yamashita, *Appl. Phys. Lett.* **2004**, *84*, 1555.

Published on the web (Advance View) February 5, 2006; DOI 10.1246/cl.2006.192