Highly Ordered Mesoporous Ni Particles Prepared by Electroless Deposition from Lyotropic Liquid Crystals

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Highly ordered mesoporous Ni particles have been prepared by electroless deposition using lyotropic liquid crystals as templates. The bath conditions, in particular the kind of the reducing agents, greatly affected the degree of the ordering of mesostructures. By using well chosen appropriate reducing agents and combining those agents, we have succeeded in synthesizing Ni particles with highly ordered mesoporosity.

Many mesoporous materials with variable compositions and morphologies have extensively been investigated.[1] The specific features of regular pore arrangement, homogeneous mesopore size, and high surface area make those materials very promising for various applications.[2] Mesoporous metals are electroconductive and the high surface area is useful as electrochemical reaction media. Several mesoporous metals including Ni[3] have been prepared after the first report by Attard et al.[4] who reported on the reduction of several metal ions in the presence of lyotropic liquid crystals made of nonionic surfactants. The mesoporous metals noted above were usually prepared by electrodeposition for the reduction of metal ions to form thin films on substrates.

Another method for the reduction of metal ions is electroless deposition, in which a reducing agent is used to produce the metal. By this method metals can be deposited homogeneously in solution in the form of a powder or a thin film depending on operating conditions. For the application to functional devices, the method of electroless deposition to form metal particles has an advantage of being a one-step process to control the particle size and morphology in addition to the formation of metal surface with unique functionalities. The electroless deposition method requires the selection of an appropriate reducing agent, which is one of the most important steps in formulating an electroless plating bath. Up to now only mesoporous Pt[4] and Pt–Ru alloys[5] have been prepared by electroless deposition.

Ni was chosen here because it is one of the metals deposited easily by an electroless method. Moreover, Ni is utilized as a catalyst,[6,7] an industrial electrolytic electrode, a fuel cell electrode,[8] and a substrate and/or current collector of battery electrodes. By choosing appropriate reducing agents we have succeeded for the first time in synthesizing highly ordered mesoporous Ni particles by electroless deposition. Here we report on the effectiveness of controlled formation of reaction nuclei and the subsequent deposition of the metal by appropriate reducing agents performed to produce a mesoporous metal of the highest quality. The meso-

structures of mesoporous metals reported so far are less ordered in almost all cases than those reported for inorganic oxides. Therefore, the present study also aimed at preparing highly ordered mesoporous metal particles by electroless deposition.

Nonionic surfactant (Brij 56, 4.0 g) was added into a solution prepared by dissolving anhydrous $NiCl_2$ (1.3 g) in distilled water (3.3 g), and the concentration of the surfactant was adjusted to be 55 wt %. The mixture was aged, and the aging process was repeated to complete homogeneous mixing. The mixture showed a homogeneous green color. Either sodium borohydride (SBH) or dimethylamineborane (DMAB) was added as a reducing agent. The color of the solution instantly changed from green to black upon the addition of SBH, indicating a very fast reduction to Ni metal particles. With DMAB, the formation of Ni metal in the bath was not observed initially, and it took 12 h for the entire solution to change its color to black.

The powder XRD pattern of the mesostructured product (before the removal of surfactant) showed a very broad peak at the low diffraction angle when SBH was used, whereas the peak was sharper when DMAB was used. Figure 1a) shows the powder XRD patterns of mesoporous Ni particles after the removal of surfactant. No peak was observed when SBH was used (pattern A), while a peak appeared at $d = 7$ nm in the pattern of the product prepared with DMAB (pattern B). The presence of the peak at such a low angle is basically in agreement with the previous report on electrodeposited mesoporous Ni films.[3]

The FE (field emission)-SEM images of the mesoporous samples are displayed in Figure 1b. The size of Ni particles obtained from the bath containing SBH was less than 100 nm (Fig-
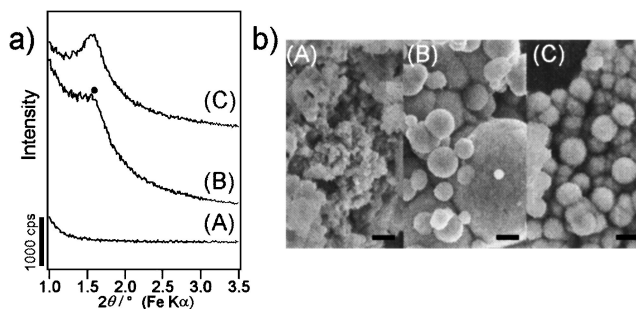

Figure 1. a) XRD patterns and b) SEM images of mesoporous Ni after removal of surfactants (A: products prepared with SBH only, B: products prepared with DMAB only, C: products prepared with both SBH and DMAB). (Scale bar: 300 nm)

ure 1b) (A)). When DMAB was used, spherical particles of 100–1000 nm in size were produced, indicating a significant influence of reducing reagents.

The ordering of the mesostructure was improved by modifying bath conditions to control the formation of Ni nuclei. When a very small amount of SBH was added into an aged DMAB bath, metal nuclei were promptly formed by the spontaneous decomposition of SBH, and subsequently the autocatalytic deposition of Ni by DMAB proceeded on the nuclei. The intensity of the low angle XRD peak of mesostructured Ni after the removal of templates was further increased (Figure 1a) (C)). Ni particles after the removal of surfactant contained ca. 2.5 wt % of carbon, indicating that the surfactant was removed substantially by ethanol. The FE-SEM image (Figure 1b) (C) shows that spherical particles of about 200–350 nm in size were produced. The particle size distribution in the case of SBH + DMAB is narrower than that found with DMAB only, though the morphologies are almost the same.

When only DMAB was used, the initial nucleation was inhomogeneous and insufficient, resulting in inhomogeneous growth of electroless deposited Ni, which lowered the ordering of the mesostructure. When a very small amount of SBH was added into the system, a sufficient amount of nuclei was formed in the initial stages, followed by homogeneous electroless deposition of Ni which proceeded with DMAB.
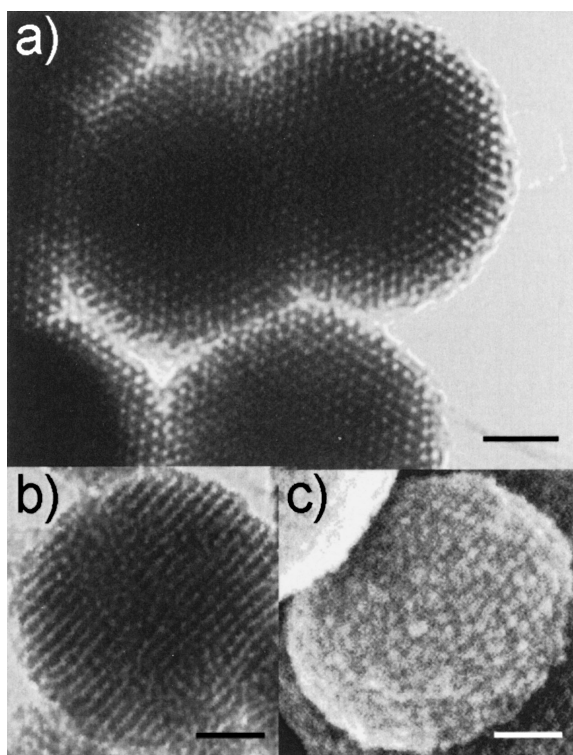

Figure 2. a), b) TEM and c) HR-SEM images of highly ordered mesoporous Ni particles prepared with both SBH and DMAB. a) TEM image of 2-*D*-hexagoal channels, b) TEM images of side view of channels, and c) HR-SEM image of side view of channels. (Scale bar: 50 nm)

TEM images of highly ordered mesoporous Ni particles prepared by using SBH + DMAB are shown in Figures 2a and b. Figure 2a clearly shows regularly arranged 2-*D*-hexagonal mes-

ochannels. Figure 2b shows mesochannels running parallel to the edge of each particle. Although there are several reported TEM images of mesoporous metals,[3,4] the ordering of those materials varies, and only a few of the TEM images show the arrangement of mesopores. The very clear TEM images presented here indicate that the highly ordered arrangement of mesopores was achieved in this study. The distance between the pores is estimated to be ca. 8 nm, which is in agreement with that calculated from the tentatively assigned (100) peak ($7.0 \times 2/\sqrt{3} = 8.1$ nm) of the XRD pattern (Figure 1a) (C)). Moreover, the first direct observation of mesoporous metal by high resolution scanning electron microscopy (HR-SEM) was achieved. Figure 2c shows the HR-SEM image of mesoporous Ni particles, indicating the presence of the arranged mesochannels consistent with those observed by TEM. In addition, On the basis of the nitrogen adsorption isotherm, the specific surface area was calculated to be 112 m^2/g (BET). The pore size distribution, as determined by BJH analysis of the adsorption curve, was in the range of 3–5 nm.

The broad peak at $2\theta = 35$–$55°$ in the high angle powder XRD pattern (not shown) is assignable to Ni (110), meaning that the pore walls are made of very minute polycrystalline Ni (fcc). Generally, the Ni deposit is of high crystallinity when the B content is lower than 2 wt %, whereas fine polycrystallites are formed when the B content is over 3 wt %.[9–12] The B content was high (ca. 5%, ICP), in line with the amorphous-like polycrystalline state of Ni.

In conclusion, we succeeded for the first time in preparing ordered mesoporous Ni particles by electroless deposition from the bath with a sophisticated combination of two reducing agents. The control of both the formation of nuclei and the deposition rate greatly affects the ordering of mesoporous metals. The method will be applicable to the deposition of various metals and alloys, which will be reported subsequently.

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