Extraction of three-dimensional silver nanostructures with supercritical fluid

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Over the last few decades, people have developed a variety of nanotechnologies for fabricating nanodevices with nanomaterials.1) Artificial metallic materials known as metamaterials have, in particular, attracted optical and materials scientists owing to their extraordinary optical properties such as negative refraction and optical cloaking.2)–4) They are basically three-dimensional in a large scale. Advanced nanofabrication technology uses either an electron, focused ion, or light beam, while such a beam is not applicable to the fabrication of three-dimensional structures.5)–7) Two-photon polymerization or photoreduction can make three-dimensional nanostructures exceeding the diffraction limit.8,9) However, it will take an enormous amount of time to fabricate such three-dimensional nanostructures over a large scale.

In our previous report, we proposed and demonstrated an unconventional nanofabrication method based on metal crystallization.10) Differently from the conventional lithographic or two-photon approach, large-scale three-dimensional structures are self-grown. An ultraviolet (UV) laser beam was used to illuminate silver nanoseeds (nanoparticles) in a solution containing silver ions and ascorbic acid. Localized surface plasmon resonance was hence excited at nanoseeds and then nanocrystals grew owing to the local heating at nanoseeds. The crystal structures looked like nanotrees with nanobranches, being dendrites with fractal geometry. Silver nanodendrites showed broadband extinction between 400 and 900 nm owing to the fractal geometry.11) We used nanodendrites as an efficient substrate for surface-enhanced Raman scattering. The only problem with this fabrication method is that silver nanodendrites bend and lie flat on substrates during the removal of the ion solution and the rinsing of structures with acetone. The nanodendrites are very thin and very fragile. In this Letter, we discuss the use of supercritical fluid for extracting nanostructures without damage.

Supercritical carbon dioxide (CO2) fluid has been used in the industry of semiconductor nanodevices and MEMS for rinsing.12) Supercritical fluid does not have surface tension, which produces capillary force. The viscosity of CO2 supercritical fluid is sufficiently small not to deform or destroy the structures in the rinsing of nanodevices by the fluid. CO2 fluid transits to CO2 gas with the decrease in pressure. As a result, nanodevices are dried and extracted.

Figure 1 shows the experimental procedure for fabricating and extracting silver nanostructures. Acetone-water (with the ratio 34 : 1) solution consisting of silver nitrate (40 mM) and L-ascorbic acid (60 mM) is added dropwise to a glass substrate. Silver nanoseeds with diameters from a few to several nm are prefixed on the substrate. The temperatures of the solution droplets and substrate are maintained at 263 K to inhibit the induction of unnecessary silver nanoparticle reduction in solution. A CW UV laser at $\lambda = 355$ nm illuminates silver nanoseeds to excite localized surface plasmon resonance, increasing the local temperature at the nanoseeds. The temperature increase triggers the growth of nanorods from nanoseeds by consuming silver ions in solution through reduction. Owing to the inhomogeneity of the distribution of the silver ion concentration surrounding the surfaces of nanorods, protrusions are grown to produce branches. Branching repeats, forming nanotrees.13,14)

The silver nanostructures in solution are put in a chamber filled with ethanol (100 mL). The acetone-water solution with silver nitrate and L-ascorbic acid dissolves in ethanol. Then, CO2 supercritical fluid is injected from the port of the chamber, while the temperature is maintained at 313 K. The pressure and flow rate of the supercritical fluid are kept at 14 MPa and 30 mL/s, respectively (the critical point of CO2 is at 304.1 K and 7.38 MPa from Ref. 15). The ethanol with the acetone-water solution dissolves in CO2 supercritical fluid and exhausts out from the other port of the chamber with CO2 gas. The flow rate of CO2 supercritical fluid is gradually reduced, and CO2 fluid transits to the gas phase. Finally, the nanostructures are extracted from the acetone-water solution without physical damage.

We have carried out an experiment of growing and extracting silver nanostructures. The results are shown in Fig. 2. Figure 2(a) shows a scanning electron microscopy (SEM) image of silver nanodendrites extracted with CO2 supercritical fluid. No structural deformation is observed. The size of this picture is $14 \times 14$ µm$^2$ (magnification of 4,000x). Figure 2(b) shows the same image as Fig. 2(a) except that the viewing angle is 45° tilted, demonstrating that the tree is three-dimensional. Figure 2(c) shows an enlarged view of part of a nanodendrite with a magnification of $27,000 \times$, where the branches of trees are ~$66$ nm thick with a gap of ~$14$ nm between adjacent branches. In comparison, a SEM image of nanodendrites extracted with liquid acetone but not with supercritical fluid is shown in Fig. 2(d). Trees lie and overlap each other on the substrate. This is due to the much higher surface tension and viscosity of acetone (23.46 mN/m

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and 0.324 mPa s at 293 K and ~0.1 MPa, respectively) than those of CO₂ supercritical fluid (0 N/m and 0.08 mPa s at 313 K and 14 MPa, respectively).\textsuperscript{16–18}

The characteristics of silver nanostructures (either spheres, rods, plates, or cubes, two-dimensional or three-dimensional, and large or small) are determined by the experimental conditions. Here, we discuss the laser power dependence of the structural characteristics (such dependence of other parameters has been discussed in our previous report).\textsuperscript{10} The UV laser beam with linear polarization is guided to silver nanoseeds on the substrate without any lenses. The diameter of the irradiation spot is 0.98 mm. If the laser power for triggering crystallization at nanoseeds is as low as 10 mW, hexagonal plates are grown as crystals [Fig. 3(a)]. In the case of low-power laser illumination, the reduction rate around nanoseeds is low, such that crystals grow slowly from nanoseeds. In such a slow reaction kinetics, a prismatic shape arises from the seeds containing planar crystallographic defects (e.g., twin planes and stacking faults).\textsuperscript{19} If the laser power is between 20 and 30 mW, three-dimensional crystals are grown as nanotrees [Figs. 3(b) and 3(c)]. As the laser power increases, the temperature at a nanoseed increases owing to the excitation of localized surface plasmonic heating on nanoseeds.

Figures 1, 2, and 3 illustrate the experimental procedure for growing and extracting silver nanostructures. Silver nanotrees are grown from silver nanoseeds fixed on the substrate in the acetone-water solution of silver nitrate and L-ascorbic acid, with UV laser illumination to induce local heating by localized plasmon resonance at nanoseeds. Nanotrees are grown in the solution, and the solution dissolves in ethanol in a chamber. CO₂ supercritical fluid is injected into the chamber, and then ethanol is replaced by the supercritical fluid. CO₂ fluid transits to the gas phase, resulting in the drying of the structure without deformation and destruction.
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