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Preparation of helical gold nanowires on surfactant tubules

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Electroless gold nanoplating of various forms of surfactant tubules yielded mono-, double- and multi-helical gold nanowires and their yarns in solution.

One of the aims of nanotechnology is to control the size and morphology of nanoparticles and nanostructured materials, while another aim is to fabricate them in an ordered structure. Various organized surfactant assemblies and polymer films have been used for these purposes.[1,2]

The size or the diameter of these nanoparticles varies from a few nm to several hundreds of nm depending on the type of metal and the method of preparation. When they are nanorods or nanowires, some of them may be several micrometers long. When we want to construct a nanoscale electric circuit, the desirable morphology should be electrically conducting nanowires.

Such an electrically conducting carbon nanotube may be a promising one for producing nanocircuits,[3] but some completely new and simple technologies to separate the electron conducting carbon nanotube from the mixture or to prepare the pure conducting carbon nanotubes are required.

Another promising nanowire is an organic one. The construction of interconnected conjugative double bonds on a 2-dimensional molecular membrane has been studied.[4] In that sense, arbitrary preparation of electron conducting organic polymers in a membrane a few nanometers thick is another important subject.

Despite all this progress, the preparation of metal nanowires is still a challenging target of nanotechnology because metal wires are expected to be easily transformed into various shapes by a nanomanipulation methods. There are basically two methods for making a metal nanowire, *viz.*, the direct preparation of a nanowire and an indirect method which consists of the conversion of an array of nanoparticles to a nanowire by a simple heat treatment.[5]

In the latter case especially, some templates for the orderly arrangement of the metal nanoparticles are required. The shape of the nanowires thus formed can be rigid straight lines, curved lines, flexible fibers, coils and others depending on the templates utilized. The accumulation of technological information for shaping the nanowires is then very important for progress in nanotechnology.

Here, we tried to prepare "helical" gold nanowires using a lipid tubule as a template. Lipid tubules have been extensively studied since their discovery by P. Yager and P. E. Schoen.[6] Electroless Ni plating of the tubule was one of the most successful strategies.[7] The tubules are known to be formed by a two-stage process.[8] First, lipid molecules aggregate to form a ribbon of bilayer membrane. The long ribbon then coils up into a tubule. Most of the lipid tubules are about 500 nm in thickness and several tens to hundreds of micrometers in length. The seams on the tubule or the edges of the ribbons are expected to provide an environment different from the other hydrophilic part of the membrane because hydrophobic alkyl chains are relatively exposed to solvent at the edge of a bilayer.

R. B. Lennox *et al*. successfully prepared polypyrrole strands by polymerizing pyrrole monomers selectively adsorbed on the edges of incomplete lipid tubules.[9] They obtained polypyrrole strands. The hydrophobicity of the alkyl chains and the electron-rich triple bonds in the surfactant structure, partially exposed to the solution are postulated to play important roles in the adsorption and reaction of the monomers at the edges.

Here, we report a new preparation of coil-shaped gold nanowires using the surfactant tubule as a template. The usually employed method for the preparation of nanoparticles or nanowires is the reduction of a metal salt in solution with an appropriate reducing agent in the presence of a suitable capping reagent. As has been reported by Burkett,[10] Au particles were discretely arranged on the tubule surface when Au nanoparticles were prepared by reducing $HAuCl_4$ in the presence of surfactant tubules. However, it is impossible to convert these discretely arranged nanoparticles to nanowires and therefore this method is not suitable for the selective preparation of metal wires on a certain portion of a solid template.

Another method of placing metal on a solid template is metal plating. Our new method consists of the nano-scale electroless gold plating of surfactant tubules. Of the many electroless plating methods, a substitution method was used. This method involves the adsorption of Sn^{2+}, reduction of Ag^+ to Ag by the Sn^{2+} (Ag plating) and substitution of the Ag with Au (Au plating).

A typical plating procedure is as follows.[11–13] Five mg of bis-phosphatidylcholine tricosadiynoyl ($DC_{8,9}PC$) was dissolved in a mixture of 5 ml ethanol and 2.14 ml water. After storing the solution at 55 °C for 12 hours, the solution was gradually cooled to room temperature to produce closed tubules. If the heating had been omitted, defective open tubules were obtained. Various combinations of the conditions gave differing forms of tubules. The solution was centrifuged and the supernatant decanted. The precipitate was then washed with water. This procedure was repeated several times. The obtained tubules were subjected to metal-plating processes. They were first dispersed in 1 ml of an accelerator solution (0.026 M $SnCl_2$ and 0.07 M CF_3COOH in methanol/water (1/1 by volume)). After reacting for 45 min, the solution was centrifuged and washed three times as described above. The obtained tubule was redispersed in 1 ml of activator (0.029 M $AgNO_3$ in ammoniacal aqueous solution) for 5 min. The separated precipitate was washed three times with water and then collected. The precipitate was dispersed in a 1 ml gold-plating solution ($[Na_3(Au(SO_3)_2] = 7.9 \times 10^{-3}$ M, $[Na_2SO_3] = 0.127$ M, [HCHO] = 0.625 M, pH = 3.0, Temp = 2 °C) and the solution was allowed to stand for 1 hour. Prolonged plating formed unnecessary Au dots on the surface of the tubules near the edges, therefore careful control of the plating time was important to produce neat nanowires. The plated sample was washed three times with pure water as described above. A TEM observation was made by using Cu grids and a JEOL 2010. When it was necessary to selectively remove the tubules from the Au-plated tubules, an excess amount of hot ethanol was added to the dispersion, and the supernatant was discarded.

Fig. 1 shows TEM images of a Au-plated closed tubule and a Au-plated open tubule (a coiled ribbon). Most of the Au particles were on a seam line or the edges of the tubules and they formed almost continuous helical lines. The lines on the tubules were confirmed to be Au by EDS (energy dispersive X-ray spectrometer) measurements of the tubular surface (Fig. 2). The Cu peaks in this chart were from the Cu-grid. When the tubule was formed from multiple ribbons, multiple helical lines were observed (Fig. 3). When the tubules were closed (Fig.1(a), Fig.3), the Au particles or wires seemed to be located under the surface of the tubular membrane.

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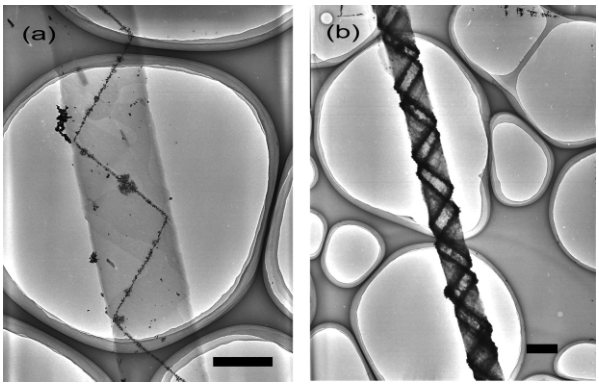

Fig. 1 TEM Images of Au-plated closed (a) and open (b) tubules. Scale bar = 500 nm.

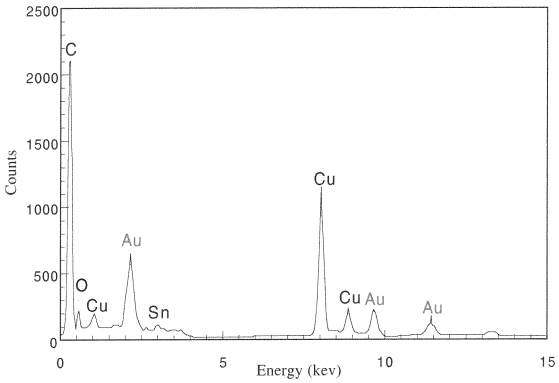

Fig. 2 Elemental analysis (EDS) of Au-plated tubules.

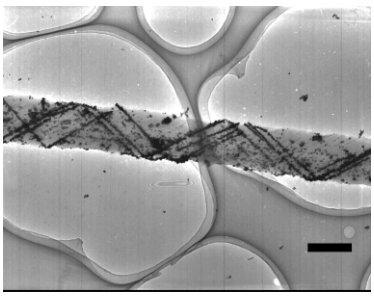

Fig. 3 TEM image of an Au-plated multilayer tubule. Scale bar = 500 nm.

They appeared to have sunk deep in the bilayer membranes of the closed tubules owing to their weight. On the other hand, Au particles thickly attached on the edges of the ribbons when the tubules were open because the edges were exposed to the solution. Moreover, the thickness of the wires on the edges increased slightly with plating time. However, a long plating time formed unnecessary Au dots on the membrane surfaces rather than on the seams.

When the templates were eliminated by extracting the surfactant with ethanol, what would be left? Do we expect scattered Au particles? Various shapes of Au wires were obtained depending on the shape of the template and the plating conditions. Some

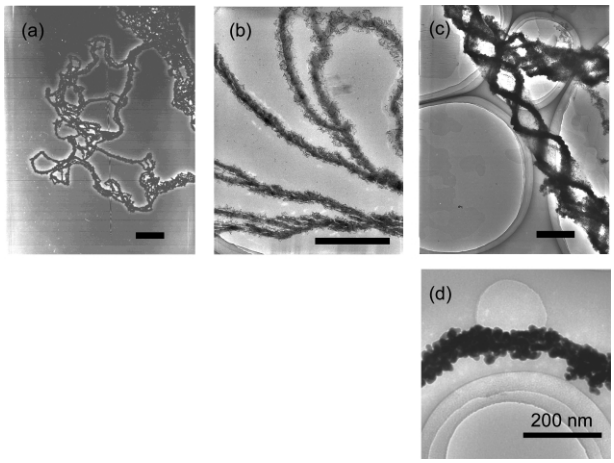

Fig. 4 TEM Images of the substances which remained after the surfactant had been removed from the Au-plated tubules. The Au wires seem to be composed of many small Au particles as is typically shown in a thick wire (d). Scale bar = 500 nm.

examples are shown in Fig. 4. When the surfactants in the closed tubules with thin Au lines on them were eliminated, entangled thin Au wires (Fig. 4(a)) or spun yarns (b), depending on the multiplicity of the ribbons, were obtained. The shapes must be due to the flexibility of the nanowires. When the surfactants in the open tubules plated for a relatively long period were eliminated, thick double helical wires were obtained (c). In the last case, the shape of the edges of the open tubules was completely copied on the shape of the Au wires. The obtained wires seem to be linear aggregates of many small particles, and would be strengthened by heat treatment at about 300 °C.

In summary, we have described a new method for preparing mono-, double- and multi-helical gold nanowires using surfactant tubules as a template in solution.

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