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Chemical Synthesis of Silver Nanowires Using *N*,*N*-Dimethyldodecylamine Oxide

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This paper describes a new approach for the synthesis of uniform silver nanowires (AgNWs) using zwitterionic amphiphile, *N*,*N*-dimethyldodecylamine oxide (DDAO). Heating of AgCl and DDAO in the presence of silver nanoparticles at 135 °C for 3 h produces longer AgNWs. The DDAO serves as a source of both a reducing and capping agent in the process.

In the past decade, considerable efforts have been devoted to producing inorganic nanowires because of their unique properties and potential application in electronic, photonic, magnetic, and sensing devices.[1–5] Silver nanowires (AgNWs) especially have attracted much attention in many technological areas because of the high electrical and thermal conductivities of bulk silver.[6–8] The one-dimensional (1-D) silver nanostructures also have unique optical and catalytic properties.[7–9]

Various chemical strategies have been applied for the synthesis of 1D inorganic nanostructure.[10] However, most strategies reported for the synthesis of AgNWs have applied a polyol method.[7,11–13] The polyol method for AgNW synthesis was originally demonstrated by Figlarz and co-workers through the reduction of $AgNO_3$ with ethylene glycol in the presence of a protective agent, poly(vinylpyrrolidone) (PVP).[14] Xia and co-workers have improved the method to obtain uniform, longer AgNWs in a high yield using a small amount of additives (including $PtCl_2$ or Fe(II)/Fe(III) species), and also revealed the continuous, simultaneous injection of $AgNO_3$ and PVP into the vessel during the reaction was effective for the better controlling of the resulting product morphology of AgNWs.[6,7]

Despite a number of reports for the standard polyol method to produce AgNWs, attempts to find alternative AgNW preparation methods have had limited success, although they are needed in order to exploit their peculiar properties and unique application. As capping agents instead of polymers, amphiphilic molecules such as cetyltrimethylammonium bromide or Aerosol OT have been used to prepare anisotropic nanocrystals of silver or other metal;[15–18] however, the resulting morphologies were rod-like, and high aspect ratio wire-like nanocrystals were scarce.

We report here the synthesis of AgNWs using *N*,*N*-dimethyldodecylamine oxide (DDAO) for the first time. The zwitterionic amphiphile, DDAO having a head group with a dipole ($N \rightarrow O$) is used as a protective agent of Ag nanoparticles, because the negatively charged oxygen atom of the head group will show an affinity for metal surfaces. The DDAO molecules also serve as a source of both a reducing and capping agent in the heating process for the 1-D crystal growth of silver. AgCl is used as a silver source of AgNWs. Our method can be conducted at a relatively high concentration of silver ($>$350 mM) compared to that of the standard polyol method (tens mM).

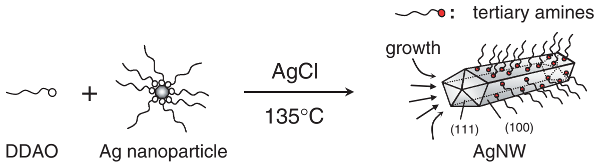


Figure 1. Schematic illustration of the experimental procedure used to produce AgNWs. Three-dimensional morphologies of AgNW showing $\{111\}$ end faces and $\{100\}$ side faces. The common fivefold axis of elongation is $\langle 110 \rangle$.

Our procedure for the synthesis of AgNWs is illustrated in Figure 1. The AgNWs were produced by heating a mixture of DDAO (0.7 g) and AgCl (20 mg) without solvent at 135 °C, where a small amount of silver nanoparticles ($<$2 wt %) were contained in order to promote the seed-mediated growth of silver.[24] Upon heating, the DDAO immediately changed to oil, and then gray, silvery precipitate of AgNWs gradually appeared in the oil. After 3 h, the reaction vessel was cooled to room temperature. The precipitate was collected and washed repeatedly with $CHCl_3$ on a filter (0.45 µm in pore size) to remove by-products such as nanoparticles and organics (The purified product contained $<$5 wt % organics, as estimated from TG analysis.). A weight of the purified AgNW was 17 mg, which corresponds to a yield of 84% based on AgCl addition.

Figures 2a and 2b show the scanning electron microscopy (SEM) images of the product prepared by our procedure. A large number of wire-like nanostructures more than tens of micrometers in length were found through the SEM observation. The nanowires have a smooth surface and a uniform diameter (ca. 70 nm) along the length, corresponding to an aspect ratio of more than ca. 1000. Figure 2c shows the powder X-ray diffraction (XRD) pattern of the nanowires. The peaks at 38.1, 44.3, 64.5, and 77.5° were assigned to the diffraction of a face-centered cubic (*fcc*) unit cell. The unit cell parameter ($a = 0.409$ nm) calculated from the peak positions corresponds closely to the value reported for bulk silver ($a = 0.4086$ nm, JCPDS file No. 04-0783). The XRD pattern shows no AgCl peaks (silver source), indicating its complete reduction to metallic silver. In addition, the higher intensity ratio of 4.3 for the (111) to (200) peaks (as compared to that of 2.5 for the bulk silver), indicates enrichment of the (111) crystalline plane in the AgNWs. Figure 2d shows the scattering spectrum obtained from the AgNW powder embedded in a thin quartz cell. The spectrum shows a broad peak with a maximum at 388 nm and a shoulder at 365 nm from the transverse plasmon modes of the 1D nanostructure of silver.[19] This differs from a plasmon peak of around 420 nm for spherical silver nanoparticles tens of nanometers in size. This also indicates that the wire-like nanostructures shown in Figures 2a and 2b were composed of metallic silver.

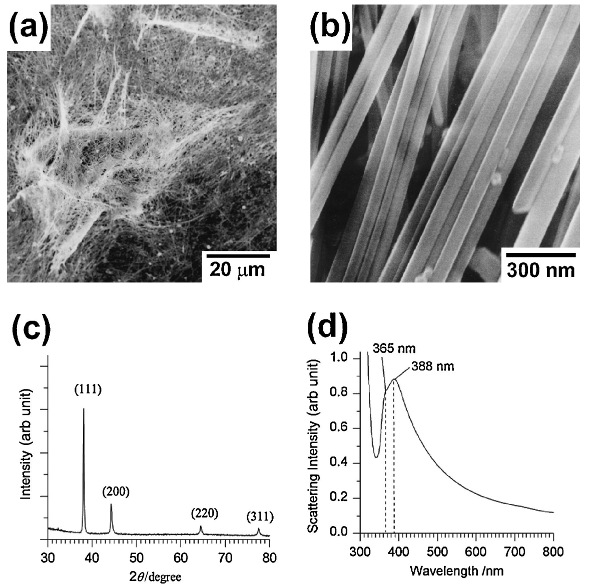


Figure 2. (a, b) SEM images of AgNWs purified through filtration and washing. (c) XRD patterns of the AgNW on a glass substrate. (d) Scattering spectrum of the AgNW powder filled in a thin quartz cell.

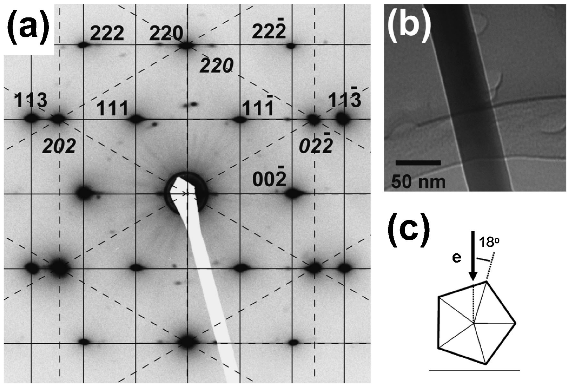
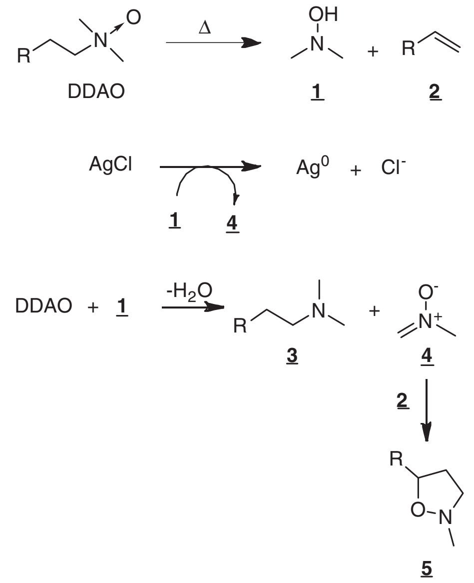


Figure 3. (a) ED pattern and (b) TEM image of a single AgNW. The ED pattern corresponds to a superposition of ⟨100⟩ and ⟨111⟩ zones of a *fcc* structure. Dashed line with Italic characters of Millers' indices: diffraction from ⟨111⟩ orientation. Solid line with Bold characters: diffraction from ⟨100⟩ orientation. (c) Illustration of a AgNW cross section, which composed of five domains and five twin boundaries. An electron beam was tilted by 18° with respective to one of the twin boundaries around the five-fold ⟨110⟩ central axis.

The electron diffraction (ED) pattern and the transmission electron microscopy image of a single AgNW were shown in Figures 3a and 3b, respectively. The defined spots of the ED pattern indicate a well-developed crystalline structure of the AgNW. The pattern consisted of a superposition of two diffraction patterns for ⟨011⟩ and ⟨111⟩ zone axis of the *fcc* structure, which were consistent with multiple twinning of 1-D nanostructures of *fcc* metals as proposed for silver nanowires, for copper rods, and for gold rods.[1,8,20,21] Regarding the plane defined by the wire axis and an incident electron beam, two different zone axis orientations were identified by rotating the wire around its axis by 18° (Figure 3c). This indicates that the AgNWs tend to grow as a bicrystal twinned at {111} planes along the common ⟨110⟩ fivefold axis to form an elongated decahedron with five {100} side faces and two ends by {111} faces as shown in Figure 1.



Scheme 1. Proposed chemical reaction in the heating process at 135 °C (R = $C_{10}H_{21}$).

We focused on the chemical reaction during the heating of the DDAO and the AgCl at 135 °C in the presence of the Ag seeds. Upon heating, the AgNW precipitate gradually appeared on the reaction vessel surface, and complete conversion of AgCl to silver metal after 3 h was confirmed by XRD (Figure 2c). Here, the ^{1}H NMR spectral data of the reaction mixture demonstrated the disappearance of the DDAO within 30 min of heating (as shown in Figure S1).[24] However, the AgNWs continued to generate over the 30 min. We therefore propose that the organic species generated by the thermal decomposition of the DDAO must induce the 1D growth of silver. Scheme 1 shows the proposed reaction that occurs during heating. The formation of *N*,*N*-dimethylhydroxyamine (**1**) and 1-dodecene (**2**) should be a preliminary reaction of DDAO pyrolysis, because aliphatic tertiary amine *N*-oxides easily decompose to olefins and *N*,*N*-disubstituted hydroxylamines upon heating, known as the Cope elimination.[22,23] We believe that the hydroxyamine **1** is responsible for reducing the AgCl to silver metal, because of the strong reducing properties of dialkylhydroxyamines. As a side reaction, along with the silver ion, the hydroxylamine **1** also reduces the remaining DDAO to form tertiary amine **3**, which is accompanied by the formation of nitrone **4**. The nitrone **4** must be trapped as isoxazolidine **5** through the reaction with the **2**. Actually, the formation of the tertiary amine **3** and the isoxazolidine **5** could be confirmed by ^{1}H NMR after their isolation from the residue according to the literature.[23,24] It is therefore proposed that the candidate for the capping agents of the silver nanocrystals during crystal growth is **3** and/or **5** after the DDAO decomposition, because amine species have the ability to coordinate to metals. The silver atoms or clusters generated on the AgCl grain surface by reduction with the reactive **4** would be capped by the **3** and/or **5** and then disperse from the grain surface to the reaction system. The silver atoms or clusters will diffuse and deposit to the seeds of silver nanocrystals through the Ostwald ripening. It is broadly accepted that the coordinative reagent kinetically controls the growth rates of metal crystals through selective adsorption and desorption on the surfaces. Therefore, the tertiary amine **3** and/or isoxazolidine **5** would induce the anisotropic growth of silver nanocrystals. The fact that the side surfaces of the AgNWs were composed of {100} facets, as shown in Figure 1, implies a higher affinity of the capping agents with the {100} facets of silver than with {111} facets of the nanowire ends.

In conclusion, we showed a new route for the synthesis of AgNWs. Our method could be conducted at a relatively high concentration of silver (>350 mM) compared to that of the standard polyol method. The AgNWs with a high aspect ratio were obtained at a high yield (>84%) by heating the AgCl and DDAO at 135 °C in the presence of silver nanoparticles without the continuous addition of the reactants using a pump. In this paper, we also proposed for the first time a possibility of tertiary amines, instead of PVP, as capping agents to direct growth of silver in a highly anisotropic 1-D manner.

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24 Materials, experimental procedure, and Figure S1 are shown in Supporting Information. This material is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.