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Synthesis of Cable-Like Copper Nanowires**

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Recently, investigation of metal nanowires has attracted much attention because of their potential use in a wide range of advanced applications. Numerous methods have been used to grow metal nanowires. Template-assisted methods are one of the synthetic strategies used most frequently, including growth inside polymer channels,^[1] alumina membranes,^[2] zeolite channels,^[3] and rod-like micelles.^[4] Also, there are quite a few reports on the formation on nanowires by crystal growth methods.^[5] Copper is of particular interest, since it shows high electrical conductivity and is suitable for potential applications such as interconnects.^[6] Interestingly, examples of forming Cu nanowires inside micelles are extremely rare. Only one related case of preparing Cu nanorods has been reported.^[7] The better-known methods to fabricate copper nanowires are electrochemical deposition of copper inside polymer channels^[1b] and anodic aluminum oxide.^[2b] To isolate the nanowires, these templates have to be removed after the growth. Here, we wish to report the synthesis of high aspect ratio copper nanowires encapsulated in poly(dimethylsiloxane) (PDMS) under mild conditions and without the use of any solvent.

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Previously, we have reported a new method to prepare Cu nanoparticles by reducing CuCl₂ with (Me₃Si)₄Si in a sealed tube at 573 K.^[8] The reaction is a two-step reduction process. As the chloride atoms are removed as chlorosilanes, CuCl₂ is first reduced to CuCl, then to Cu metal. Further investigations by varying the reaction conditions have shown that, in addition to Cu nanoparticles, the presence of Cu nanowires in low quantities is common. A typical transmission electron microscopic (TEM) image is shown in Figure 1a. In addition to aggregates of nanoparticles, high aspect ratio nanowires can be observed. The diameter is in the range of 20–80 nm and the length can be as large as 10 μm. An enlarged TEM image of a typical wire with a diameter of 20 nm is shown in Figure 1b. From the selected area electron diffraction (SAED) pattern shown in Figure 1c, the lattice parameter *a* is estimated to be 0.36 nm, close to the value of Cu metal.^[9] In addition, the nanowires are bicrystals (twin crystals), and two zone axes [0,1,1] and [1,1,1] are identified. A high-resolution (HR) TEM image (Fig. 1d) of a wire shows that the longitudinal direction is [0,2,2]. From the images, we conclude that the wires have a Σ9 [011] (35.2°) twin structure.^[10] It should be noted that there is a layer of amorphous material, estimated from the image to be 5–10 nm thick, encapsulating the wire. From the energy dispersive X-ray (EDX) spectrum (Fig. 1a), the presence of Si and O atoms is evident. Although the signal of C is obscured by the carbon support, we tentatively assume that the amorphous surface layer encapsulating the wire is polyorganosiloxane, formed as a by-product from the reactants and the hydroxyl groups on the surface of the reaction vessel. In order to improve the yield of the Cu nanowires, we have tested many reaction conditions by combining various ratios of the reactants, reaction temperatures, and pressures. However, the improvement was limited. We considered also the possibility that the presence of the polyorganosiloxane polymer might play an important role in the nanowire formation. A series of reactions was performed to obtain more indications. First, highly purified CuCl (99.99 %) with an average crystal size of 60 μm was allowed to react with (Me₃Si)₄Si in a sealed Pyrex tube, which had been flame-dried before use. Presumably, the rigorous drying process of the reaction apparatus would hinder the formation of the polyorganosiloxanes. In this experiment, we found the process did prohibit the formation of Cu nanowires. In the next experiment, in addition to the highly purified CuCl and (Me₃Si)₄Si, some common PDMS (Dow Corning 200R Fluid) heating oil was also added to the reaction volume. Through the same heating process, improved yields of copper nanowires were found in the products. Thus, the experiment using the oil supports the theory that coating the CuCl surface with a layer of PDMS might play an important role. In order to examine the effect of PDMS, we changed the oil for Dow Corning DC 976, a frequently used PDMS high-vacuum grease with a high molecular weight and high viscosity. The yield of Cu nanowires increased significantly. In Figure 2, scanning electron microscopy (SEM) and TEM images of a sample are shown. From the images, the yield of the nanowires is estimated to be over 50 %, a signifi-

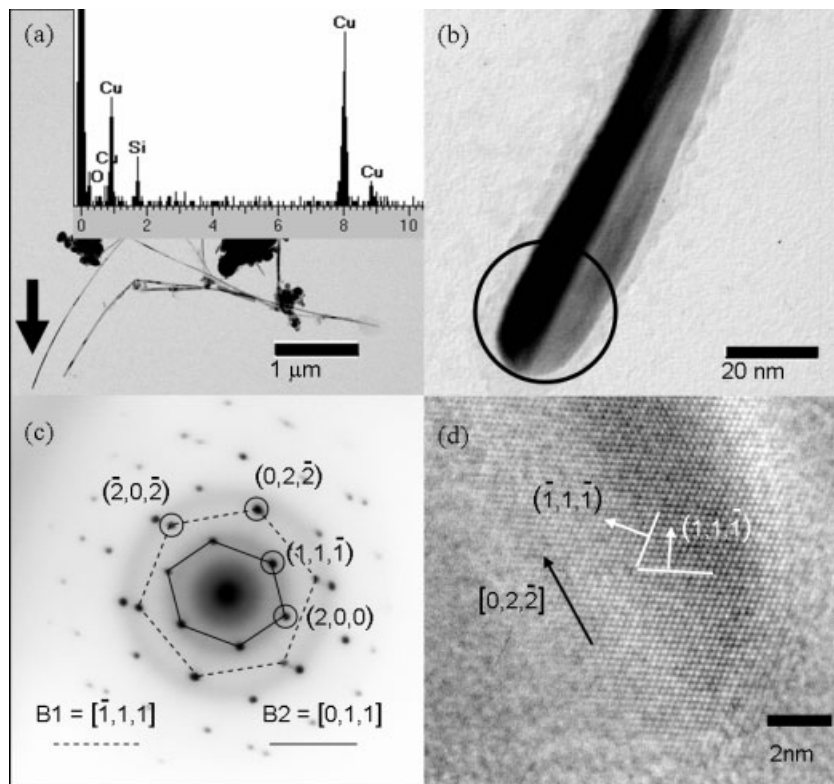


Fig. 1. Images of a sample prepared by reacting CuCl_2 with $(\text{Me}_3\text{Si})_4\text{Si}$ at 473 K. a) TEM image and EDX spectrum. b) Enlarged view of the marked area in (a). c) SAED of (b) in the marked area. d) HRTEM of a copper nanowire.

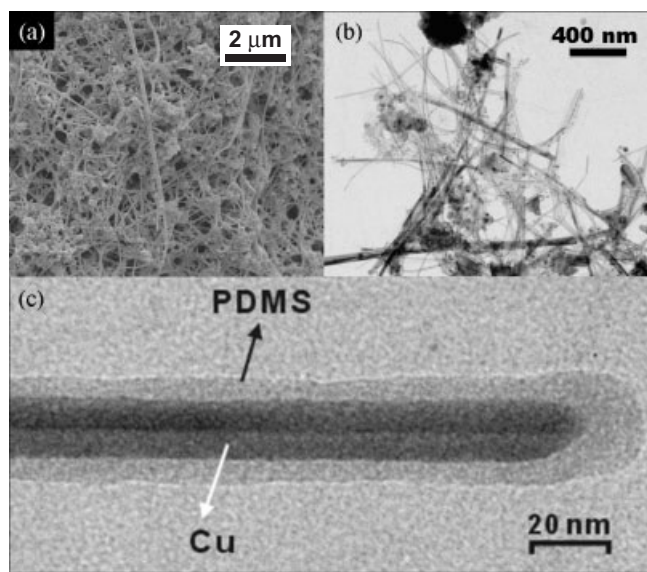


Fig. 2. Images of a sample prepared by reacting CuCl with $(\text{Me}_3\text{Si})_4\text{Si}$ in the presence of PDMS (Dow Corning High Vacuum Grease DC-976) at 473 K. a) SEM, b) TEM, and c) enlarged TEM view of a Cu wire.

cant improvement over the other conditions mentioned previously. In the SEM studies, the magnification is limited because the samples were charged (Fig. 2). The insulating PDMS sheath of the cable-like nanowire is clear in the TEM image shown in Figure 2c.

Apparently, the process resembles the vapor-liquid-solid (VLS) mechanism frequently employed to explain the growth of many nanowires.^[11] However, the phenomena observed in this study differ from the traditional VLS mechanism in the following ways. In a typical VLS process, the constituents of the nanowires are frequently evaporated from a solid source and nucleated on nanosized liquid phase catalysts at high temperatures. In our work, the ingredient of the nanowires, Cu, was from a solid phase reactant CuCl . At the reaction temperature of 473 K, CuCl ($m_p=703$ K, $b_p=1763$ K) does not vaporize or melt. Thus, the process could neither be a physical vapor deposition (PVD) nor a chemical vapor deposition (CVD). Also, no catalysts were added in the reaction to assist the growth. The nucleation process must be different from the common VLS mechanism. So, how could the Cu atoms in CuCl be assembled into the nanowire structure? Here, a different growth model, vapor-solid reaction growth (VSRG), based on the observations, is proposed in Figure 3 to rationalize the results. Previously, an analogous pathway has been proposed for the growth of Cu_2S nanowires from Cu.^[12] In step 1, the

$(\text{Me}_3\text{Si})_4\text{Si}$ molecules diffuse across the PDMS layer to reach the CuCl surface. After adsorption and surface reaction steps to remove the Cl atoms as chlorosilanes, the Cu atoms are reduced from the oxidation state +1 to 0. These unstable surface Cu atoms may aggregate into more stable nanosized Cu clusters.^[13] It is well known that nanosized metal particles freeze at temperatures significantly lower than the normal melting

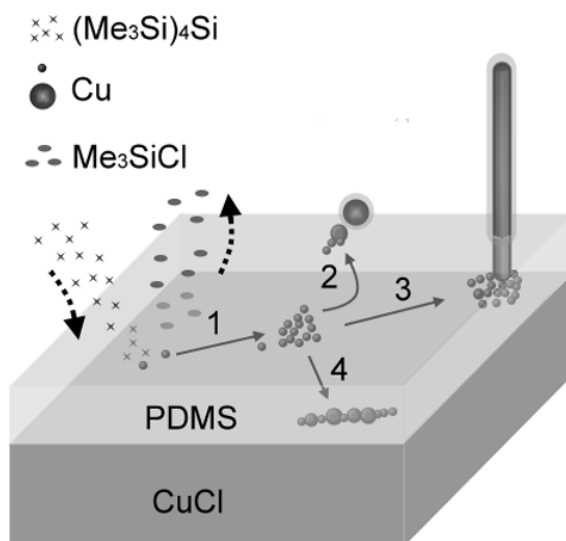


Fig. 3. Proposed reaction pathways.

points of bulk materials.^[14] At the reaction temperature 473 K, many of the Cu nanoclusters should be in the liquid state. They could diffuse on the surface,^[15] coalesce with each other^[16] and grow either isotropically into large particles (step 2) or anisotropically into wires (step 3 and step 4), as shown in Figure 3. In our study, it appears that whether the growth follows the isotropic or the anisotropic route is highly affected by the presence of PDMS. Without the addition of extra PDMS, more nanoparticles than nanowires were obtained. The yield of nanowires increased as the quantity and the molecular weight of PDMS were increased. The exact role of PDMS is yet to be fully understood. Presumably, it functions as a soft template to confine the newly formed Cu nanoparticles in a limited space. When the quantity of PDMS is relatively high and the molecular weight is large, the nanoparticles are less likely to leave the surface of CuCl. Also, the surface can be viewed as an anisotropic environment, with more polymers in the horizontal than in the vertical direction. The growth of the diameter in the horizontal direction is more restricted, while the growth of the length in the vertical direction is less constrained. The reason is that the polymers exert less resistance on the growing Cu particles in the vertical than in the horizontal direction. The difference provides a tendency for the diffusing nanoclusters to coalesce and crystallize anisotropically into a uniform nanowire, as shown in the third step. On the other hand, nanowires may be solidified from connected nanoparticles, as shown in the fourth step. However, the wires formed from this process would be polycrystalline with uneven diameters. This was not observed in the study. Thus, the process is less likely to be the growth mechanism.

In conclusion, we have discovered an interesting new method to grow cable-like Cu nanowires encapsulated in PDMS in high yields at low temperatures. The VSRG process is a simple solvent-free reduction of solid CuCl by vapor phase $(\text{Me}_3\text{Si})_4\text{Si}$. Further investigation is in progress to obtain better understanding of the growth mechanism and better products by controlling the reaction conditions. The application of this strategy to other metals is also under investigation.

Experimental

Preparation of Cu Nanoparticles from CuCl_2 : CuCl_2 (purity 98 %, 0.10 g, 0.74 mM) was mixed with $(\text{Me}_3\text{Si})_4\text{Si}$ (0.18 g, 0.56 mM) and ground in an agate mortar. The pulverized powder was collected and sealed into a Pyrex tube (6.6 mm diameter, 34 cm length) under vacuum. In a tube furnace, the sealed tube was ramped to 473 K in 10 min and then held at this temperature for 6 h.

A solution of Dow Corning High Vacuum Grease DC976 (2 mL) dissolved in tetrahydrofuran (100 mL) was prepared. The solution (5–15 mL) was added to CuCl (99.99 % purity, 0.10 g, 1.0 mM) in a Pyrex tube. The volatile components in the mixture were removed under vacuum. After $(\text{Me}_3\text{Si})_4\text{Si}$ (0.18 g, 0.56 mM) was added, the tube was sealed under vacuum and placed in a tube furnace. The temperature was ramped to 473 K in 10 min and kept for 6 h.

The samples were washed by hexane to remove reaction by-products. For SEM studies (JEOL JEM-6330F at 10 kV), the samples on carbon tapes were coated with a thin layer of gold (~5 nm) before being inserted into the SEM chamber. A drop of the samples, dispersed in hexane by ultrasonic treatment for 5 min, was placed on a carbon film coated copper grid for TEM (JEOL JEM-2000FX2 at 200 kV) and HRTEM (JEOL JEM-2010F at 200 kV) studies.

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Metallic Sub-Nanometer $\text{MoS}_{2-x}\text{I}_y$ Nanotubes

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Recently synthesized $\text{MoS}_{2-x}\text{I}_y$, ($0 \leq x < 1$, $y < 1$), assigned in our first report as $\text{MoS}_2\text{I}_{1/3}$ nanotubes,^[1] represent the smallest known inorganic nanotubes. They were synthesized by the catalytic transport reaction using C_{60} . Their sub-nanometer-sized diameters and perfect crystal growth enable the self-assembly of these nanotubes at different length scales. The nanotubes group into bundles composed of a few nanotubes up to several hundreds of thousands of nanotubes, forming a nanotube crystal. The bundles can easily decompose to very narrow assemblies and even to individual nanotubes. Here,

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