

行政院國家科學委員會專題研究計畫 期中進度報告

奈米金屬及金屬化合物之合成(1/3)

計畫類別：整合型計畫

計畫編號：NSC91-2113-M-009-020-

執行期間：91年08月01日至92年07月31日

執行單位：國立交通大學應用化學系

計畫主持人：裘性天

報告類型：精簡報告

報告附件：出席國際會議研究心得報告及發表論文

處理方式：本計畫涉及專利或其他智慧財產權，1年後可公開查詢

中 華 民 國 92 年 5 月 26 日

Two communications have been written and submitted for publication.

1. Attachment 1, submitted to *J. Am. Chem. Soc.*, in revision.

In-Situ Generation of Silica Shell Layer - Key Factor to Simple High Yield Synthesis of Silver Nanowires

2. Attachment 2, submitted to *Chem. Comm.*

New nanotube synthesis strategy- application of sodium nanotubes formed inside anodic aluminium oxide as a reactive template

See attached files.

In-Situ Generation of Permethyilsiloxane Polymer Soft Template - Key Factor to Simple High Yield Synthesis of Cable-Like Silver Nanowires

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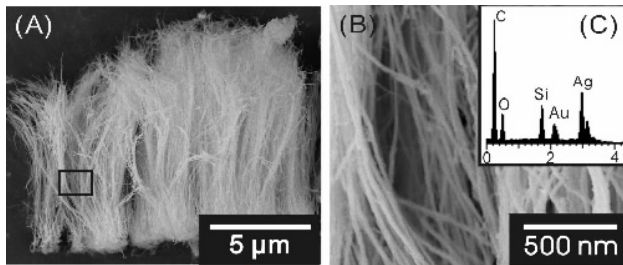
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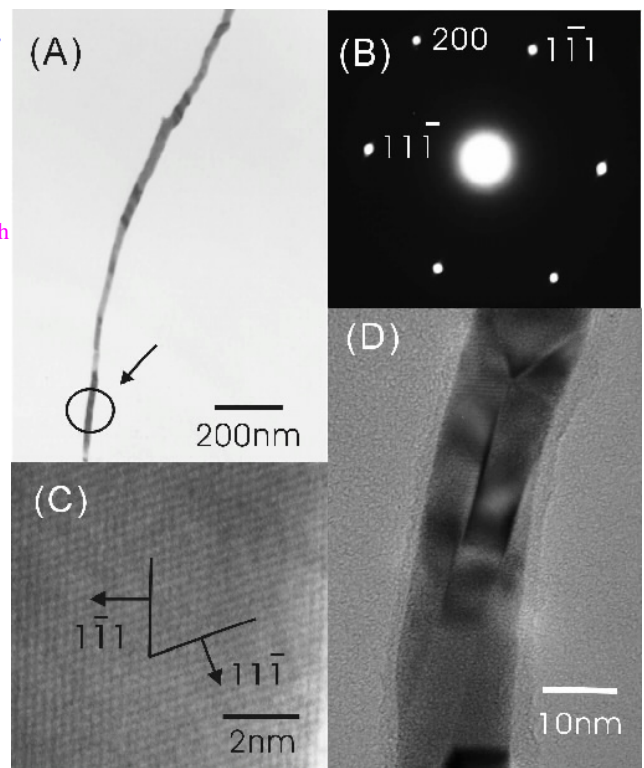
Synthesis of silver nanowires is an area under intensive investigation.¹ Many methods have been explored, frequently, including hard and soft template are needed to assisted shape formation of these nanowires, and electrochemical reduction.^{ref [1-3]} Previously, we have reported that addition of polydimethylsiloxane (PDMS) to a new solvent free vapor solid reaction growth (VSRG) method process assisted to prepare cable like Cu nanowires formation significantly in good yield by reacting polydimethylsiloxane (PDMS) coated CuCl with (Me₃Si)₄Si in sealed tubes^[4] Also, we have demonstrated the importance of polymeric shell in controlling the electron beam induced growth of Cu nanowires.³ The reaction is a vapor solid reaction growth (VSRG) and a plausible mechanism has been proposed to elucidate the growth process. Here, we wish to report a simple high yield synthesis of Ag nanowires Unlike other literature processes,⁴ the polymer soft template found in this observation is generated *in situ* in the reaction We are curious whether employing the VSRG strategy to synthesize other metal nanowires is possible. After some exploration, we wish to report another VSRG example, a simple high yield synthesis of cable like Ag nanowires via a parallel process which is much simpler than the processes reported before.³

Reacting AgNO₃ and (Me₃Si)₄Si in a sealed tube under low



pressure at 400K (Caution: The reaction generates gaseous byproducts. The tube should have enough volume to allow their expansion so that the pressure will not build up excessively inside. The gas escaping the tube turned brown in air).^{ref [5]} After workup, it was found that AgNO₃ was converted nearly quantitative into metallic silver, as determined by X ray diffraction (XRD). The XRD peaks were indexed to a facecentered cubic (fcc) material. The lattice constant *a*, calculated from the diffraction pattern, was 0.4090 nm, close to the reported value of Ag, *a* = 0.4086 nm.^{[5], [6]} Fig. 1a shows a scanning electron microscopic (SEM) image of the product. It contains bundles of nanowire with an average length of ca. 10 μm. An enlarged image (Fig. 1b) shows that the

nanowires have a mean diameter of 25 ± 5 nm. It is estimated that the density of our nanowires is smaller than which synthesized by template strategies, such as AAO and calix[4]hydroquinone nanotubes.³ An energy dispersive spectrum (EDS), shown in Fig. 1c, suggests that in addition to sample holder tape Ag, the sample contains Si O and Ca. Also A typical transmission electron microscopic (TEM) image of a nanowire is shown Fig. 2a



While the overall wire structure is shown in Fig. 2B, indicates a polycrystalline structure. The SAED pattern, shown in Fig. 2b, indicates that the marked area is within the domain of a single crystal. From the dot pattern, the lattice

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that the marked area is within the domain of a single crystal. From the dot pattern, the lattice parameter is estimated to be crystal. From the dot pattern, the lattice parameter a is estimated to be 0.42 nm, closed to the reported value of A_{51}^{56} . A high resolution TEM (HRTEM) image of the area is shown in Fig. 2c. The directions of two plans (11,1) and (1,1,1) are identified, showing that the included angle of 70.1° is close to the theoretical value of 70.5° . The {111} d spacing was measured to be 0.24 nm, close to the value estimated from the literature data, 0.233 nm. As shown in Fig. 2d, a layer of amorphous material, with a thickness of 1–3 nm encapsulating the wire, is observed. Based on the EDS data, the layer is tentatively identified to be a permethylsiloxane polymer (PMSP), formed as a high molecular weight byproduct formed *in situ* from the reaction.

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This layer, probably acting as a soft template, and assisted the nanowire growth via VSRG via the VSRG pathway proposed before.^{15,5}

major the silica O-Si-O 1255 cm^{-1} and 1100/1070 cm^{-1} Si(CH₃)₂ 820² and 480² cm^{-1} . In addition to the absorptions of silica, signals assignable to OSiMe groups

α -silica PMSP at 844 cm^{-1} , CH₃ deformation at 1384 cm^{-1} , Si-O bending at 805 cm^{-1} , and Si-O rocking at 443 cm^{-1} . In addition to the absorptions of silica, signals assignable to OSiMe groups solution. The key factor to this simple process is the *in situ* formation of the PMSP layer. The material is formulated based on the following information. From preliminary analysis of the volatile byproducts by gas chromatography-mass spectrometry (GC-MS) and infrared spectroscopy (IR), (Me₃Si)₂O, (Me₃SiO)₂Si and other permethylsiloxane oligomers were found. Detection of these lower molecular weight products suggests that higher molecular weight portion might also be formed in the reaction. IR of the bulk solid product confirmed the presence of peaks assignable to PMSP. Based on the TEM, EDS and IR data, we conclude that the Ag nanowire is enclosed in a PMSP shell. The role of (Me₃Si)₄Si in the reaction is important. It acts as the reductant. The atom Si bonded with four trimethylsilyl groups is important, because it will form Si-O-Si crosslinking structures which make siloxane inflexible. We have tried the reaction of AgNO₃ and (Me₃Si)₆Si, a reductant with a similar chemical reactivity,² but the yield of silver nanowires is lower

than the reaction of AgNO₃ and (Me₃Si)₄Si. In preliminary analysis, the shell of reaction AgNO₃ and (Me₃Si)₆Si is polydimethylsiloxane (PDMS), a flexible structure.

the oxygen scavenger capable of removing oxygen atoms from the nitrate group, as well as the source of PMSP. In addition to the siloxanes, NO was detected. When the sealed reaction tubes were opened and exposed to air, a brown vapor was immediately formed. This observation suggests that NO, which turned into NO₂, was in the byproducts.⁷ (Revised to here)

Other mechanisms could not rationalize the growth properly. In a typical Vapor-Liquid-Solid (VLS) process, the mechanism used most frequently to rationalize the growth of many nanowires, components of the nanowires are evaporated and nucleated under the assistance of a nanized liquid phase catalyst at high temperatures. In this work, no catalysts were added to assist the growth. In addition, at the employed reaction temperature of 400 K, the solid phase reactant AgNO₃ (m.p. = 485 K) neither melted nor evaporated. Therefore, the whole process differs from the VLS condition considerably. Also, the process could neither be a physical vapor deposition (PVD) nor a chemical vapor deposition (CVD). It could not be a simple thermal decomposition of AgNO₃ either because the reaction temperature was much lower than the temperature of decomposition of AgNO₃, 713 K. The discussion above has ruled out many unlikely growth mechanisms.^{16,62}

In contrast, many similarities exist between this study and our previous preparation of Cu nanowires.⁴ In both reactions, (Me₃Si)₄Si was employed to react with solid metal compounds under overall comparable reaction conditions. The only significant difference is that the cable sheath material, PDMS in the Cu case was not added in this study. Instead, the polymeric layer enclosing the Ag nanowires was a reaction byproduct generated *in situ*. From preliminary analysis of the volatile byproducts by GC-MS and infrared spectroscopy, (Me₃Si)₂O, (Me₃SiO)₂Si and other permethylsiloxane oligomers were found. Detection of these lower molecular weight byproducts supports the formulation of the polymeric shell outside the Ag nanowires to be PMSP. The role of (Me₃Si)₄Si in the reaction is important. It acts as the reductant, the oxygen scavenger capable of removing oxygen atoms from the nitrate group, as well as the source of PMSP. In addition to the siloxanes, NO was detected. When the sealed reaction tubes were opened and exposed to air, a brown vapor was formed immediately. This observation suggests that NO, which turned into NO₂, was in the byproducts.^{17,1}

In conclusion, we have discovered a remarkably simple one-step solvent free method to synthesize bundles of like Ag nanowires in high yield. The reaction is another example of VSRG of nanowires. Exploration of other possibilities is in progress.

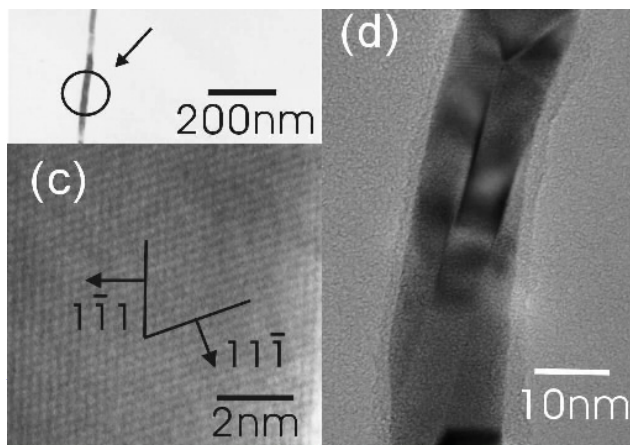
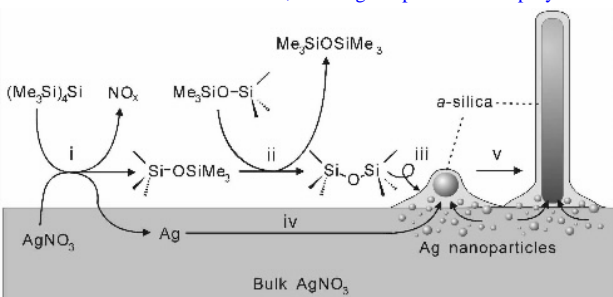


Figure 2 a) TEM image of a silver nanowire b) SAED of the marked area in (a). c) HRTEM image of the marked area in (a). d) TEM image of a silver nanowire, showing the presence of a polymeric shell.



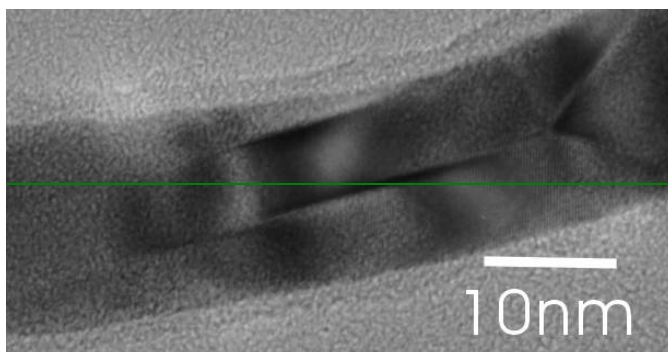
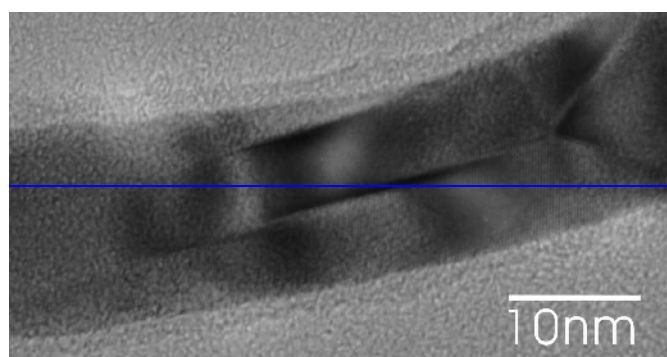
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Experimental

Synthesis of Silver Nanowires. Manipulation of chemicals was performed under an oxygen-free environment. Crystals of AgNO_3 (0.10 g, 0.59 mmol, Fisher Scientific) and $(\text{Me}_3\text{Si})_4\text{Si}$ (0.10 g, 0.31 mmol)^{18f} were manually pulverized together into powders in an agate mortar. The powders were collected and sealed into a Pyrex tube under vacuum (Caution: The reaction generates gaseous byproducts. The tube should have enough volume to allow for their expansion.). In a tube furnace, the sealed tube was ramped to 400 K in 10 min and held at the temperature for 2 h. After the tube was opened (Caution: Vapor phase byproducts produced in the reaction may cause a pressure build up in the tube. The byproducts escaped from the tube turned brown when they encountered air, indicating the formation of NO_2), the samples were washed by THF and dried at 400 K to remove reaction byproducts. The solid products on carbon tapes were coated with a thin layer of gold (~5 nm) and characterized by SEM (JEOL JSM 6330F at 15 kV). Also, the samples on carbon film coated copper grid were investigated by TEM (JEOL JEM 2010 at 200 kV) and HRTEM (Philips TECNAI 20 at 200 kV).

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