

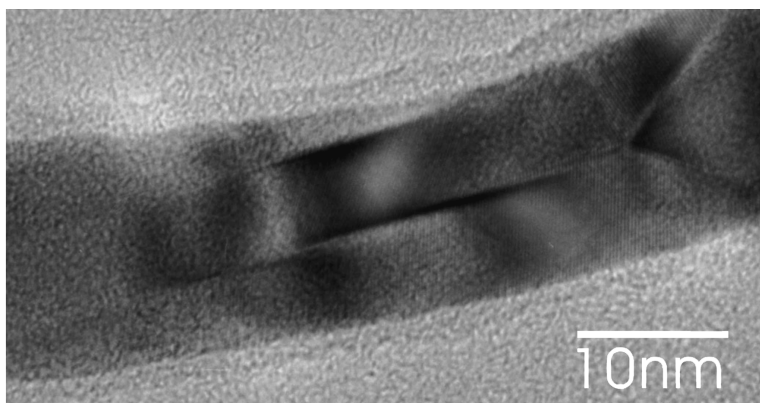
Communication

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to the Simple High Yield Synthesis of Silver Nanowires**

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

Chih-Hao Hsia,[†] Ming-Yu Yen,[†] Chu-Chun Lin,[†] Hsin-Tien Chiu,^{*,†} and Chi-Young Lee[‡]

Department of Applied Chemistry, National Chiao Tung University, Hsinchu, Taiwan, 30050, R.O.C., and
Materials Science Center, National Tsing Hua University, Hsinchu, Taiwan, 30043, R.O.C.

Received March 27, 2003; E-mail: htchiu@cc.nctu.edu.tw

The synthesis of core–shell nanowires is an area under intensive investigation for their potential technology applications.¹ Many methods have been explored, and, frequently, hard and soft templates are needed to assist shape formation of these nanowires. Previously, we have reported that addition of poly(dimethylsiloxane) (PDMS) to a solvent-free vapor-solid reaction growth (VSRG) process assisted Cu nanowire formation significantly.² Here, we report our discovery of a simple high yield synthesis of Ag nanowires. Unlike other literature processes,³ the key step in this preparation is the in situ generation of a silica shell layer.

AgNO₃ and (Me₃Si)₄Si were reacted in a sealed tube under low pressure at 400 K (*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.)⁴ After workup, a black solid was isolated. It did not dissolve in organic solvents such as THF and ethanol. It could be suspended in them briefly but precipitated quickly. As determined by X-ray diffraction (XRD), it was found that AgNO₃ was converted nearly quantitatively into metallic silver. The XRD peaks were indexed to a face-centered cubic (fcc) material. The lattice constant *a*, calculated from the diffraction pattern, was 0.409 nm, close to the reported value of Ag, *a* = 0.4086 nm.⁵ Figure 1A shows a scanning electron microscopic (SEM) image of the product. It contains bundles of nanowires with an average length of ca. 10 μm. An enlarged image (Figure 1B) shows that the nanowires have a mean diameter of 25 ± 5 nm. The diameter of the nanowires does not vary with a change in the reaction temperature from 400 to 475 K. The density of the nanowires is lower than that of those synthesized using templates, such as AAO and calix[4]-hydroquinone nanotubes.^{3d,g} An energy dispersive spectrum (EDS), shown in Figure 1C, suggests that in addition to signals of the carbon tape and the sputtered Au layer, the sample contains Ag, Si, and O. A typical transmission electron microscopic (TEM) image of a nanowire is shown in Figure 2A. While the overall wire structure is polycrystalline, a selected area electron diffraction (SAED) pattern, shown in Figure 2B, indicates that the marked area is within the domain of a single crystal. From the dot pattern, the lattice parameter *a* is estimated to be 0.42 nm, close to the reported value of Ag.⁵ A high-resolution TEM (HRTEM) image of the area is shown in Figure 2C. The directions of two planes (1, -1, 1) and (1, 1, -1) are identified, showing that the dihedral 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 Figure 2D, a layer of amorphous material, with a thickness of 1–3 nm encapsulating the wire, is observed. An as-prepared sample was studied by X-ray photoelectron spectroscopy (XPS). The survey spectrum showed that the photoelectron intensity ratios of Si to

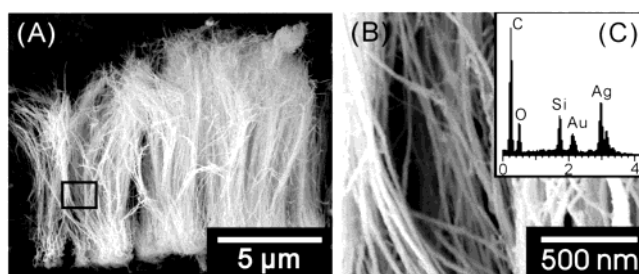


Figure 1. (A) SEM image of silver nanowires. (B) Enlarged view of the marked region in (A). (C) EDS of the marked region in (A).

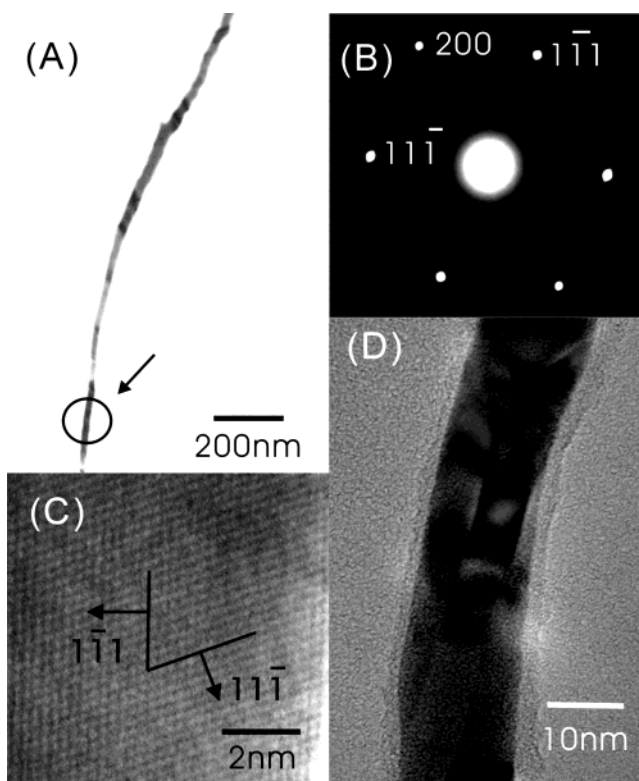


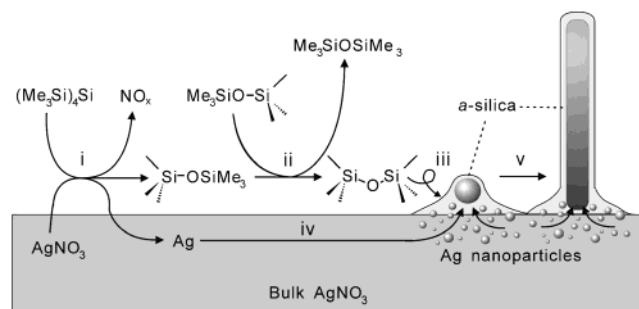
Figure 2. (A) TEM image of a silver nanowire. (B) SAED of the marked area in (A). (C) HRTEM image of the marked area in (A). (D) TEM image of a silver nanowire, showing the presence of a shell layer.

Ag and O to Ag were high. After Ar ion sputtering, the ratios decreased significantly. High-resolution XPS spectra showed Si 2p, Ag 3d_{5/2}, and O 1s electrons at 102.8, 368.3, and 532.5 eV, respectively. These are assigned to the elements in silica and Ag metal.⁶ On the basis of the XPS and the TEM data, we conclude that the external layer of the wires is amorphous silica (*a*-silica) formed in situ.

[†] National Chiao Tung University.

[‡] National Tsing Hua University.

Scheme 1. Proposed Reaction Steps To Form α -Silica Shell Encapsulated Ag Nanowires



An infrared spectroscopic (IR) study of the sample showed the absorptions originated from Si–O bonds at 1070 (Si–O stretching), 805 (Si–O bending), and 443 cm^{-1} (Si–O rocking).⁷ In addition to the absorptions of silica, signals assignable to OSiMe groups were also detected, including 1384 and 1255 (C–H deformation) and 844 (Si–Me stretching) cm^{-1} . Elemental analysis showed that the sample contained C (3.263 wt %) and H (0.994 wt %). After Ag was dissolved in a nitric acid solution, the shell was separated and estimated to be ca. 18 wt % of the solid. We suggest that the α -silica shell contained OSiMe₃ groups terminated silsesquioxane structures.⁸ Gas chromatography–mass spectrometry (GC–MS) and IR showed that N₂O, (Me₃Si)₂O, (Me₃SiO)₄Si, and other permethylsiloxane oligomers were produced as byproducts also. When the sealed reaction tube was opened and exposed to air, a brown vapor was formed immediately. This observation suggests that NO, which turned into NO₂, was likely to be a byproduct.⁹

Generation of the α -silica layer appears to be one of the key factors to this simple process. Other nanowire growth mechanisms could not rationalize the discovery reported here properly. In a typical vapor–liquid–solid (VLS) process, one of the most frequently mentioned nanowire growth mechanisms,¹⁰ components of the nanowires are evaporated and nucleated under the assistance of a nanosized 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, AgNO₃ (mp = 485 K) neither melted nor evaporated. Therefore, the whole process differs from the VLS condition considerably. Moreover, the process could neither be a physical nor a chemical vapor deposition. It could not be a simple thermal decomposition of AgNO₃ either because the reaction temperature was much below the temperature of decomposition of AgNO₃, 713 K. The discussion above has ruled out many unlikely growth mechanisms. Our previous preparation of Cu nanowires, produced via a VSRG process, was carried out under conditions comparable to this study.² The significant difference is that, in this report, the shell material α -silica was generated in situ while poly(dimethylsiloxane)s was added ex situ as a soft template in the growth of Cu nanowires. The growth pathway of the Ag nanowires is proposed in Scheme 1 and discussed below. In (i), the reaction between (Me₃Si)₄Si and AgNO₃ forms Ag atoms and siloxane oligomers. Through (ii) and (iii), the oligomers polymerize via condensation reactions into the silica shell which may act as a template in the process. As shown in (iv), the Ag atoms combine into clusters and nanoparticles. By diffusion and coalescence with others, the nanoparticles combine into a nanosized crystal. In (v), the final step, the nanocrystal grows anisotropically into a nanowire as more nanoparticles incorporate into it. Appar-

ently, the growing silica shell controls and confines the nanowire growth. Employing (Me₃Si)₄Si in the reaction appears to be important to the silica formation. It is possible that the quaternary Si atom of (Me₃Si)₄Si assists forming Q type siloxane units,¹¹ the building block of silica. In contrast, using (Me₂Si)₆, a chemically comparable silane oligomer,¹² to react with AgNO₃ produced Ag quantitatively but with much lower nanowire yield. Preliminary analysis indicated that PDMS was generated as the shell material. Apparently, oxidation of (Me₂Si)₆ favors producing D type siloxane units,¹¹ the building block of PDMS. It is a structurally flexible template which cannot control the nanoparticle growth direction effectively.

In conclusion, we have discovered a remarkably simple one-step solvent-free method to synthesize bundles of core–shell Ag nanowires in high yield. One of the key factors to the simplicity is the in situ generation of the α -silica shell layer. The exploration of other possibilities is in progress.

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Supporting Information Available: SEM, TEM, XRD, IR, and XPS data of the nanowires. GC–MS and IR of the byproducts. TEM of the shell (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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