

## Synthesis of Silver Nanowires by Reduction of Silver-Pyridine Complexes

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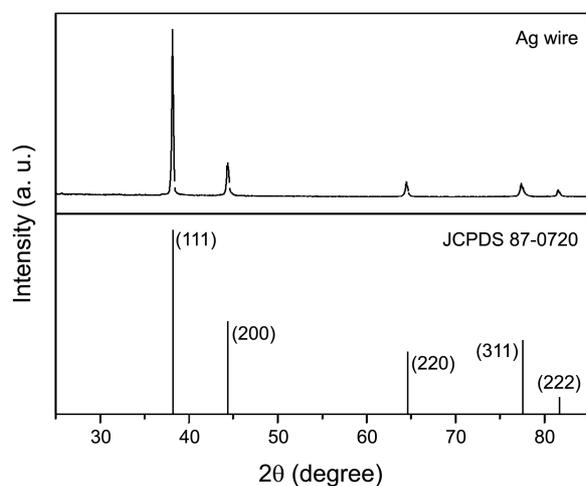
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One-dimensional (1-D) metallic nanostructures, such as wires, rods, and tubes, have unique electrical, optical, and thermal properties, and potential applicability in microelectronics, optoelectronic devices, and sensors.<sup>1-3</sup> Since silver is the metal with the highest electrical ( $6.3 \times 10^7 \text{ S}\cdot\text{m}^{-1}$ ) and thermal ( $429 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ ) conductivities, it has been widely used as conductive interfaces in electronics.<sup>4-6</sup> Silver nanowires are therefore being studied for the next generation of nanoelectronics, solar cells, and sensors.<sup>7-10</sup> Many methods have been developed to prepare silver nanowires within hard templates, such as anodic aluminum oxide (AAO), carbon nanotubes, and co-polymers.<sup>11-15</sup> However, the subsequent removal of the templates is difficult. The nanowires' sizes are also limited to the hard templates' pore size. Therefore, wet chemical methods capable of the large-scale production of silver nanowires without hard templates are required. Soft template-assisted methods have been used for the preparation of silver nanowires, with poly(vinylpyrrolidone) (PVP) used as a soft template and ethylene glycol used as both a reducing agent and solvent.<sup>16-18</sup> This work reports a simple interfacial method using cetyltrimethylammonium bromide (CTAB) as a soft template for fabricating straight and ultra-long silver nanowires with lengths of up to 50  $\mu\text{m}$  and diameters of about 50-300 nm.

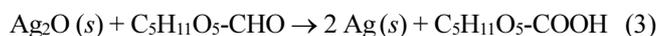
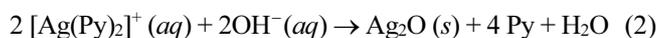
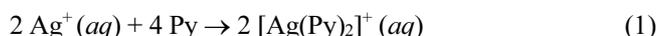
Powder X-ray diffraction (XRD) patterns of the silver products prepared using the  $\text{AgNO}_3/\text{CTAB}/\text{pyridine}/\text{glucose}/\text{water}/\text{cyclohexane}$  system at 120  $^\circ\text{C}$ .



**Figure 1.** XRD patterns of silver products prepared using a  $\text{AgNO}_3/\text{CTAB}/\text{pyridine}/\text{glucose}/\text{water}/\text{cyclohexane}$  system at 120  $^\circ\text{C}$ .

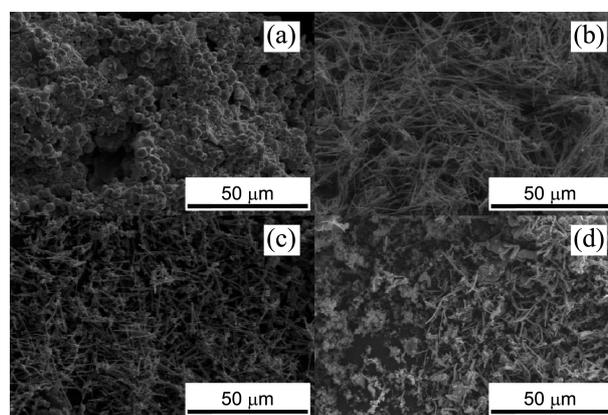
water/cyclohexane system showed peaks corresponding to those reported for bulk silver (JCPDS 87-0720,  $a = 0.4077 \text{ nm}$ ) with a face centered cubic (fcc) structure without any impurities (Figure 1). The intensity ratio of (111) to (200) of 4.9 is much larger than the theoretical value of 2.2, indicating that the intensity of the (200) peak was much smaller than expected. The XRD data suggest that the silver nanowires grew preferentially along the [100] direction.

Pyridine (Py) was used as a ligand for the silver ions ( $\text{Ag}^+$ ) to form a silver-pyridine complex,  $[\text{Ag}(\text{Py})_2]^+$ , which was pH 9.2 in aqueous solution. This complex reacted with  $\text{OH}^-$  in basic solution and  $\text{Ag}_2\text{O}$  was formed through dehydration. Silver nanowires were then produced by reduction with glucose at the interface between the aqueous solution and cyclohexane solvent. The silver nanowires were formed by:

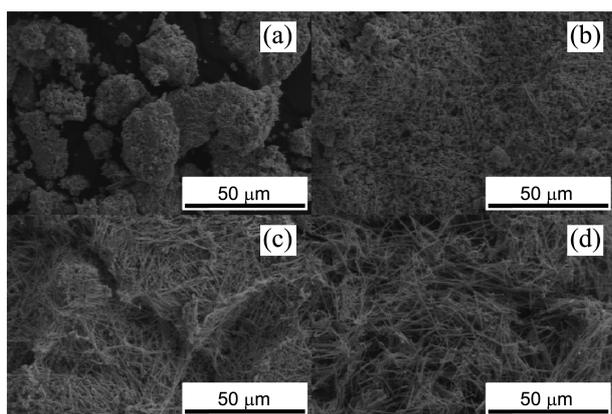


Scanning electron microscopy (SEM) showed that the silver products prepared from the silver-pyridine complex depended on the reaction temperature (Figure 2). At 80  $^\circ\text{C}$  and 120  $^\circ\text{C}$ , silver microparticles and silver nanowires were formed. The nanowires' lengths decreased with increasing reaction temperature above 160  $^\circ\text{C}$ ; the longest nanowires were obtained at 120  $^\circ\text{C}$ .

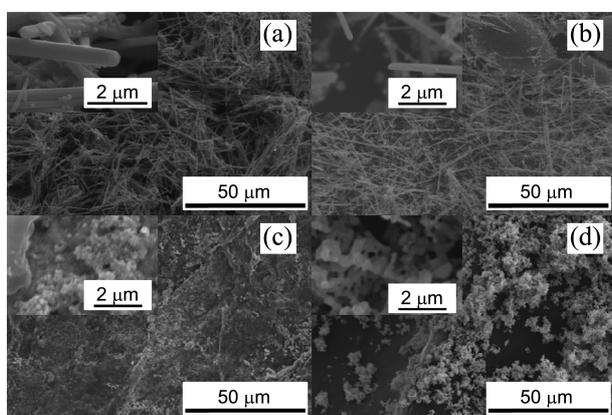
The effects of ligand concentration were assessed through



**Figure 2.** SEM images of the silver products prepared using pyridine at: (a) 80  $^\circ\text{C}$ , (b) 120  $^\circ\text{C}$ , (c) 160  $^\circ\text{C}$ , and (d) 200  $^\circ\text{C}$ .



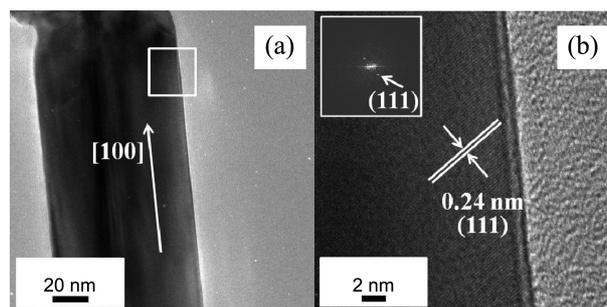
**Figure 3.** SEM images of silver products prepared at 120 °C using pyridine at molar ratios relative to silver ions of: (a) 10, (b) 20, (c) 40, and (d) 80.



**Figure 4.** SEM images of silver products prepared using various ligands in  $\text{AgNO}_3/\text{CTAB}/\text{ligand}/\text{glucose}/\text{water}/\text{cyclohexane}$  systems at 120 °C: (a) pyridine, (b) aniline, (c) ammonia, and (d) trimethylamine.

adding different amounts of pyridine to a fixed concentration of silver ions. SEM images were recorded after reactions at 120 °C (Figure 3). A 10:1 molar ratio of pyridine to silver ion resulted in aggregated nanoparticles; a 20:1 molar ratio gave nanowires with aggregated nanoparticles; and above 40:1, only silver nanowires were obtained. Ultra-long silver nanowires up to 50  $\mu\text{m}$  in length were prepared when the molar ratio of pyridine to silver ion was 80:1.

SEM showed that the silver products varied with the type of ligand used in the  $\text{AgNO}_3/\text{CTAB}/\text{ligand}/\text{glucose}/\text{water}/\text{cyclohexane}$  system (Figure 4). Pyridine and aniline ligands generated appropriate amounts of silver nanowires. Simple silver nanoparticles were obtained from ammonia or trimethylamine ligands. Therefore, the ligand significantly affected the formation of silver nanowires, with pyridine and aniline being suitable for the formation of silver nanowires and ammonia and trimethylamine being unsuitable. The silver-ligand complexes likely arranged and self assembled linearly due to  $\pi$ - $\pi$  interactions between the aromatic rings of the silver-ligand complexes. The hydrophobic parts of CTAB were arranged parallel to the layer of nonpolar cyclohexane. At the interface between the aqueous solution and



**Figure 5.** (a) HRTEM images of silver nanowires prepared using pyridine at a molar ratio relative to silver ions of 80 at 120 °C. (b) High-magnification HRTEM images of a silver nanowire's edge parallel to its longitudinal axis. Inset (b) shows the FFT pattern of an individual silver nanowire.

the cyclohexane, silver-ligands could be stabilized by the CTAB soft template. The silver nanowires likely formed by the reduction of silver-ligand complexes at the interface.

Sun *et al.* demonstrated the polyol processing of silver nanowires using PVP soft templates.<sup>16,19</sup> PVP macromolecules interacted more strongly with the {100} planes of the silver nanowires' sides than with their terminal {111} planes. This resulted in anisotropic crystal growth along the [100] direction of the nanowires. High-resolution transmission electron microscopy (HRTEM) characterized the silver nanowires prepared at 120 °C from silver-pyridine complexes with an 80:1 molar ratio of pyridine to silver (Figure 5). Higher magnification HRTEM images were recorded of the edge parallel to the longitudinal axis of an individual nanowire. The individual nanowire was shown to be *ca.* 80 nm wide. The observed lattice spacing of 0.24 nm corresponds to the (111) plane. Fast Fourier transform (FFT) patterns were recorded of an individual silver nanowire corresponding to the lattice fringe (Inset, Figure 5(b)) This indicated that the single crystalline silver nanowires were formed.

Ultra-long silver nanowires up to 50  $\mu\text{m}$  in length and diameters of about 50-300 nm were prepared by the reduction of a silver-pyridine complex solution through reactions at a water/cyclohexane interface. Glucose was used as a reducing agent and CTAB as a soft template. Aromatic ligands were important in the formation of the silver nanowires that grew along the [100] direction.

## Experimental Section

$\text{AgNO}_3$  (Aldrich, 99.0%), pyridine (Aldrich, 99.8%), aniline (Aldrich, 99%), ammonium hydroxide (Aldrich 28%), trimethylamine (Aldrich, 99.0%), cyclohexane (Aldrich, 99%), cetyltrimethylammonium bromide (TCI, CTAB, 95%), and glucose (Aldrich, 99.5%) were used as received. In a typical synthesis of silver nanowires using a  $\text{AgNO}_3/\text{CTAB}/\text{pyridine}/\text{glucose}/\text{water}/\text{cyclohexane}$  system, 6.8 mL pyridine and 2 mmol glucose were added to 1.0 mL 1.0 M aqueous  $\text{AgNO}_3$  under stirring for 5 min. 1.6 g CTAB and 40.0 mL cyclohexane were then added under stirring for 1 h. The reaction solution was transferred to a 100 mL Teflon-lined

autoclave and heated at 120 °C for 24 h. The system was then allowed to cool to room temperature. The product was obtained by filtering, washing several times with ethanol, and drying at 60 °C for 12 h. The effects of pyridine concentration on the formation of silver nanowires was assessed by preparing mixtures with various molar ratios of pyridine to silver ion by adding different amounts of pyridine to a fixed concentration of silver ions. Ligand effects were assessed by reacting pyridine, aniline, ammonia, and trimethylamine at 120 °C at a fixed 80:1 molar ratio of ligand to silver ions.

The structures of the silver products were analyzed by powder X-ray diffraction (XRD, PANalytical, X'pert-PRO-MPD) using Cu K $\alpha$  radiation. Products' morphologies were characterized by scanning electron microscopy (SEM, Hitachi S-4300) and high-resolution transmission electron microscopy (HRTEM, JEOL JEM-3010).

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