# Formation of Silver Nanowires by a Novel Solid−Liquid Phase Arc Discharge Method

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One-dimensional (1D) nanostructured materials have attracted considerable interest of recent scientific research due to their unusual properties and potential applications.[1−8] Carbon nanotubes have been prepared by an arc discharge evaporation technique[1,2] or by thermal decomposition of benzene vapor[9] or by the template techniques such as a template carbonization technique using an aluminum oxides film.[10,11] Recently, several approaches have been reported to insert metal into the nanotubes prepared by the arc-discharge evaporation technique.[12−16] Kyotani and co-workers have reported the preparation of platinum nanorods and nanoparticles in uniform carbon nanotubes obtained by a template carbonization method.[17] Exploration of novel methods for synthesis of the 1D nanostructured metal materials is a challenging research area.

In this communication, we report a novel method for preparation of silver nanowires via a so-called solid−liquid phase arc discharge method (SLPAD). It was found that aging time following the SLPAD method has a significant effect on the formation and growth of the silver nanowires.

The apparatus of the SLPAD method was presented in Figure 1. High-purity silver filaments (ca. 1.5 mm in diameter) were used as two electrodes. One of the electrodes was dipped into the 0.1 mol/L $NaNO_3$ solution. The end of another silver electrode was momentarily brought into contact with the surface of the $NaNO_3$ solution while a certain voltage (ca. 150V) was used between the two electrodes using an ac step-down circuit. It formed the instantaneous circulation between the two electrodes and arc discharge sparks at the point end of the latter silver electrode. This resulted in a continuous dissolution of the silver electrode into the solution due to the great exothermic heat releasing during the arc discharge. A silver colloidal solution was produced. The apparatus was cooled with water. After the colloidal solution was aged for several days, precipitates obviously appeared. The precipitates were washed with distilled water and absolute ethanol, and dried in a vacuum at 60 °C for 2 h. UV−vis absorption spectrum was recorded with a Shimadzu UV-200 spectrophotometer at room temperature. The X-ray powder diffraction (XRD) pattern was determined at a scanning rate of 0.02° $s^{-1}$ in $2\theta$ ranging from 10° to 80°, using a Japan Rigakn D/max $\gamma_A$ X-ray diffractometer with graphite monochromatized Cu Kα radiation ($\lambda$ = 0.154178 nm). TEM images were taken with a Hitachi model H-800 transmission electron microscope, using an accelerating voltage of 200 kV.

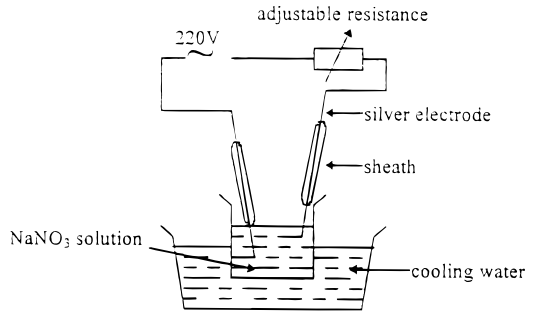


**Figure 1.** The apparatus of the solid−liquid phase arc discharge method (SLPAD).

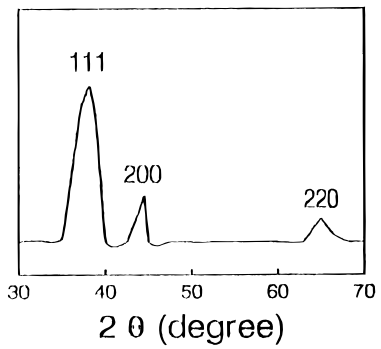


**Figure 2.** XRD pattern of the Ag nanowires obtained by aging for 3 days the solution treated by the SLPAD method.

The UV−vis absorption peak of the resulting solution treated by the SLPAD method was found at about 302 nm, which illustrates the existence of Ag clusters. Figure 2 shows the XRD pattern of the product obtained by aging the solution for 1 week. All the peaks in the XRD pattern can be indexed as face center cubic (fcc) Ag phase with cell parameter $a$ = 0.40805 nm, which is close to the reported data (JCPDS File No. 4-0783). The

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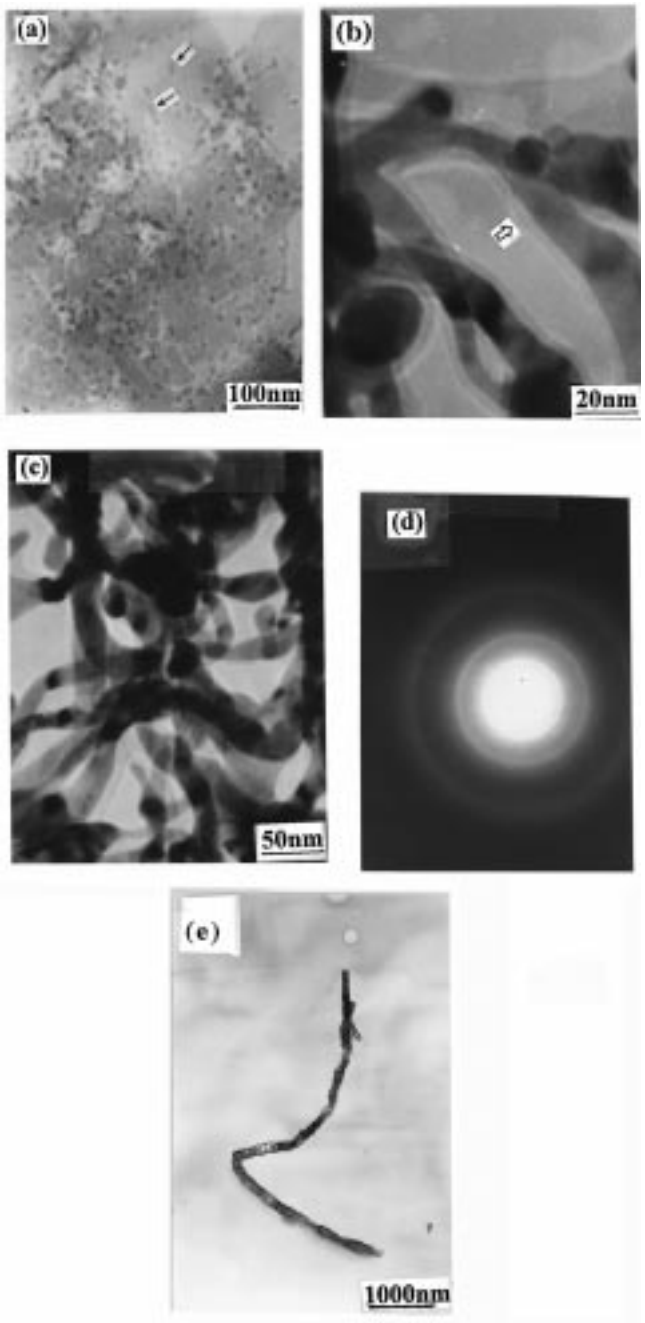


**Figure 3.** The TEM images of the products obtained by the SLPAD method. Aging time is (a) 30 min, (b) 3 days, and (c) 1 week, respectively. (d) The corresponding electron diffraction (ED) pattern for (c); (e) Aging time is 2 weeks.

observation of the resulting solution reveals that no obviously visible precipitate appeared at the beginning of the aging process. A TEM image (Figure 3a) of the solution aged for 30 min shows that the solution contains many tiny column-like particles with average size of 15 × 5 nm. If the aging time is prolonged, the black precipitate will present itself. Figure 3b shows the typical morphology of the product obtained by aging the solution for 3 days, which demonstrates that silver nanowires with 5−15 nm in diameter and the lengths up to 100 nm have formed. A layer of shaded area encircles the nanowires, as shown by an arrow in Figure 3b. The results show that no diffraction ring appears in the electron diffraction (ED) pattern for the corresponding selected area, indicating that the shaded area may be an amorphous phase. We believe that those shaded areas are comprised of the aggregated silver clusters in the solution, which have insufficient time to crystallize well. A typical TEM image of the product obtained by aging the solution 1 week was shown in Figure 3c. It shows the nanowires with a diameter of 10−20 nm and a length up to 1 $\mu$m. Compared with the product obtained by aging the solution for 3 days, no shade area is observed for the product obtained by aging the solution for 1 week. It proves that the Ag clusters crystallized well on the surface of the nanowires in the late process of longer aging time, which thickened and elongated the nanowires. Figure 3d shows the ED pattern for the silver nanowires in Figure 3c, which demonstrates that the Ag nanowires are polycrystalline. When the aging time is prolonged to 2 weeks, the nanowires grew to be larger, with a typical size of 80 nm in diameter and 14 $\mu$m in length, as shown in Figure 3e. It seems that the nanowire is composed of several nanowires which are linked together, resulting in the nonuniform structure of the nanowire.

The possible formation process of the silver nanowires is proposed. The above results suggest that the aging process following the SLPAD method plays a key role in the formation of silver nanowires. It is well-known that the arc discharge released great exothermic heat, leading to the occurrence of the continuous dissolution of silver electrodes in a form of silver clusters. These clusters entered into $NaNO_3$ solution in a possible shape of the tadpole-like or column-like morphology, as shown by the arrows in Figure 3a, which may be due to their gravity and surface tension. In addition, the cooling water will restrain the contraction of these shaped clusters and prevented them from becoming spherically shaped. These factors may be favorable for the formation of the Ag nanowires. The formation and growth process of silver nanowires can be illustrated as following:

$$\text{Ag (electrodes)} \xrightarrow{\text{SLPAD}} \text{Ag (clusters)} \xrightarrow{\text{aging}} \text{Ag (nanowires)}$$

The detailed formation mechanism of the Ag nanowires needs to be investigated further.

In summary, a novel solid−liquid phase arc discharge method (SLPAD) was successfully developed for preparation of silver nanowires. It was found that the aging time following the SLPAD method plays a key role in the formation and growth of silver nanowires. The possible formation process of the Ag anowires was proposed. The present technique may be extended to prepare other metal nanowires.

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