Wet Chemical Synthesis of Ag Nanowires Array at Room Temperature

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This letter describes a new simple method to prepare silver nanowires array in solution phase by direct chemical reduction at room temperature. In the process no seeds and no stabilizers are needed.

One-dimentional (1D) nanostructures (wires, tubes, and rods) are expected to play an siganificant role in fabricating nanoscale devices. Metal nanowires have been the focus of many recent studies because of their potential use as active components or interconnects in fabricating electronic, photonic and sensing devices.[1,2] Bulk silver has excellent electronic and thermal conductivities among all the metals. As a result, the synthesis and characterization of silver nanowires recently attracted great attention from a broad range of researchers. Silver nanorods and nanowires have been prepared by ultraviolet irradiation–photoreduction, solid–liquid phase arc discharge,[3] a pulsed sonochemical method.[4] Several direct solution-phase approaches to silver nanowires by chemical reduction in the presence of functional polymers[5–7] or surfactants[8] and other "soft templates"[9–12] have been explored. However, these methods are often characterized by adscititious seeds and stabilizers or elevated temperature ($>100\,^{\circ}\mathrm{C}$).[5,13] Moreover, silver nanowire arrays have not been obtained directly by chemical reduction in solution phase. Highly ordered arrays of metallic nanowires are expected to play an essential role for interconnects and high-density magnetic storage devices because of their unique electrical and magnetic properties.[14,15] One promising technique for the intergration of nanowires into well-defined architectures is their deposition into ordered templates. But most of the metallic nanowires (cobalt, copper, iron, etc.) were synthesized by electrodeposition in porous templates.[16] The diameters of the rod or wire-shaped nanoparticles can be varied by using template membranes with different pore diameters. Piao and Kim successfully synthesized AgI nanowires[17] by the ion reaction between Ag^+ and I^- in anodic alumina oxide (AAO) membrane, and the diameter of the wires can be controlled by the diameters of the used template. Herein, we developed a relatively new and simple method to prepare Ag nanowires array through chemical reduction of Ag^+ by BH_4^- in AAO template (Ag^+ is reduced by BH_4^- rapidly and Ag deposited in the pores.). Different from the above methods stated, no seeds and stabilizer are needed. Furthermore, the synthesis was conducted at room temperature.

Anodic alumina oxide (AAO) membrane (thickness 60 µm) was purchased from Whatman Corp. The diameter of the pore is 200 nm averagely. The membranes were cleaned for 10 min in an ultrasonic water bath. $AgNO_3$ (analytical reagent) and $NaBH_4$ (analytical reagent) were purchased from Beijing chemical factory and used without further purification. An apparatus shown in Figure 1 was constructed and manufactured using PTFE for the synthesis of Ag nanowires array.

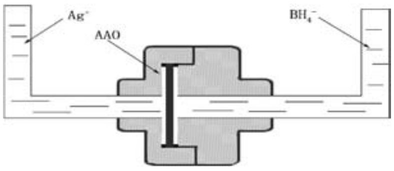

Figure 1. The apparatus constructed for the synthesis of Ag nanowires array.

In a typical synthesis, 0.02 mol/L of $AgNO_3$ and 0.02 mol/L of $NaBH_4$ aqueous solutions of the same volume were poured into the glass tubes from different sides, respectively. AAO was placed in the center of the equipment and its edge was sealed by two rubber gaskets, which can keep the two different solutions from blending by leaking out through the clearance. Then, both ions Ag^+ and BH_4^- diffused into the pore of AAO membrane from different direction owing to the presence of concentration difference of solutions, which applied as a driving force for the ionic diffusion. Ag^+ and BH_4^- would enter and meet in the pore of the AAO membrane. Ag^+ was reduced by BH_4^- rapidly in situ, and Ag was obtained. Thus each pore of AAO membrane served as a reaction vessel. In this process, Ag obtained in the initial stage formed nanoparticles, and the nanoparticles grew up gradually and connected each other with the reaction going along, which can be rectified by SEM images at different stages. After completion of the reaction, the Ag/AAO composite was thoroughly washed with deionized water. Then the resulting composite was immersed in 10 wt % H_3PO_4 for 4 h at room temperature to remove the alumina membrane, and the bare bundles of nanowires were cleaned by a large amount of distilled water and ethanol. When the concentration of the solution was changed to 0.06 mol/L and 0.08 mol/L, the similar results were obtained.

Field emission scanning electron microscopic (FE-SEM, S-4300FEG equipped with Energy dispersive X-ray) images of the prepared Ag nanoparticles at different stages are shown in Figure 2. In the short reaction time (1.5 h), only small nanoparticles of Ag were found (Figure 2a). It was attached on the wall of AAO separately. When the process continued to 12 h, nanorods can be observed (Figure 2b). After 24 h, silver nanowires can be obtained (shown in Figure 2c). The diameter of the nanowires was approximately 200–250 nm, equal to the pore diameter of the alumina membrane, and the length was about 60 µm. Besides that, the AAO template with an average pore diameter of 100 nm (100 ± 40 nm) was also used to prepare Ag nanowires. For the obtained Ag nanowires, their diameters were about 100 nm. And the morphologies had no obvious difference.

The composition of as-prepared Ag nanowires was characterized by energy dispersive X-ray spectroscope (EDX). The

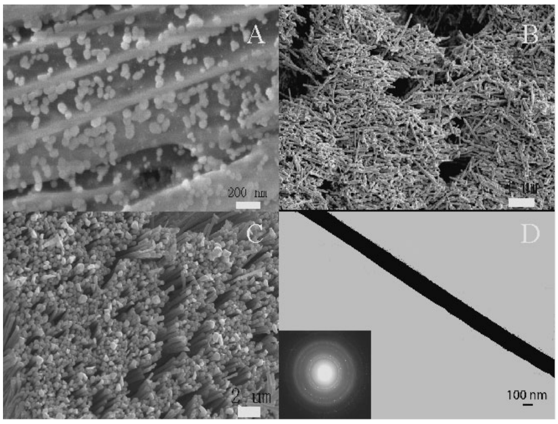

Figure 2. SEM images of the prepared Ag nanoparticles at different stages of the reaction. A (1.5 h); B (12 h); C (24 h); D: TEM image and electron diffraction pattern of a single as-prepared Ag nanowires.

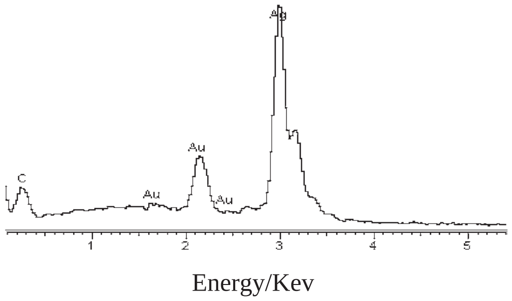

Figure 3. The EDX spectroscopy of as-prepared Ag nanowires.

EDX spectroscopy confirmed the presence of Ag, carbon and gold in the nannowires (Figure 3). Before SEM measurement, the samples were stick to the sample stage by electric adhesive and then coated with a thin gold film to improve the conductivity. So, the EDX spectrum shows the presence of Au. The carbon was from carbon adsorption under the electron beam irradiation and electric adhesive. Figure 2d displays representative TEM (JEM-200CX) images and the selected area electron diffraction pattern of a single Ag nanowire, which indicated the single Ag nanowire has polycrystalline nature. It was coincident with the images taken from the growing process of Ag nanowires shown in Figure 2.

In summary, we developed a new simple and rapid method to prepare Ag nanowire arrays with high yields. The diameter of the as-prepared Ag nanowires can be controlled by the pore diameter of the membrane. Furthermore the process carried through at room temperature and no adscititious seeds was added. The reaction condition was easy to control. This method can also be used to prepare 1D organic and inorganic core-shell nanostructure and their arrays. We have successfully filled AgI nanowire in pyrrene nanotube by this method.[18]

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