COMMUNICATION

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Paired cell for the preparation of AgI nanowires using nanoporous alumina membrane templates†

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This communication describes a relatively new and simple method for the preparation of AgI nanowires using nanoporous alumina membrane templates which can be easily extended to prepare nanowires of many other materials.

During the past two decades, potential applications in electronic, optical, electrooptical devices and sensors have prompted much research interest in the preparation and processing of nano-sized materials.[1–5] Nano-sized materials can exhibit electronic and optical properties somewhat different from identical bulk materials because of their quantum tunable-electronic properties as a result of the so-called quantum size effect.[6–12]

Bulk AgI is a well-known superionic conductor.[13–18] AgI-based superionic conductors have very high ionic conductivity compared with other monovalent cation conductors, although the ionic radius and mass of Ag ion are larger than those of, for example, Li ion. Several methods have been developed to produce nano-sized AgI.[19–22] Previously, the preparation of AgI nanowires was achieved by electrochemical deposition of silver in nanoporous templates, followed by chemical reaction of I_2 with silver nanowires.

Porous alumina membranes are prepared electrochemically from aluminium metal and have been studied for many years. The pore structure of a porous alumina membrane is a self-ordered hexagonal array of cells with cylindrical pores of almost uniform diameter and length.[23–27] In recent years, porous alumina membranes have been widely used to confine the growth of nano-sized materials due to their remarkable hardness, uniform pore size and high pore density.[28–32]

In this communication, we report on a new and simple method for the preparation of AgI nanowires in nanoporous alumina membrane templates using aqueous solution system for the first time, to the best of our knowledge.

Fabrication of AgI nanowires was carried out using the process shown schematically in Fig. 1. A high-purity plain aluminium foil (thickness 250 μm, purity > 99.99%, Aldrich) was used as a starting material. Highly ordered and perforated nanoporous alumina membrane templates were prepared by a two-step anodization technique as described previously.[26] The thickness of the as-prepared porous aluminium membrane was 40 μm. Chemical treatment of the membrane was performed in 5 wt% H_3PO_4 at 35 °C for 16 min to widen the pores. The diameter of the pores was approximately 70 nm.

A paired cell was constructed using two Teflon half-cells and was separated by the nanoporous alumina membrane (Fig. 1(a)). $AgNO_3$ and KI aqueous solutions of the same volume and the same concentration were poured into each half-cell as shown in Fig. 1(b). The experiment was then left for about 48 h at room temperature. During this stage, Ag^+ and I^- would enter and meet in the alumina nanopore to form AgI nanowires. Thus, each pore of alumina membrane served as a reaction vessel. The experimental results showed that the reaction between Ag^+ and I^- was limited in the porous alumina membrane.

After completion of the reaction, the resulting AgI/Al_2O_3 composite was thoroughly washed with deionized water. Then, the resulting composite was immersed in 5 wt% H_3PO_4 at 35 °C for 1 h in order to partly remove the alumina membrane and for 3 h to remove the membrane substrate completely. The remaining AgI nanowires were rinsed several times in deionized water.

Field emission scanning electron microscopic (FE-SEM; Jeol JSM 6700F) images of the prepared porous alumina membrane and the AgI nanowires are shown in Fig. 2. The porous alumina membrane showed well-ordered hexagonal arrays of cylindrial pores with a pore density of 1×10^{10} cm^{-2} (Fig. 2(a)). It was seen in the typical cross-sectional micrograph (Fig. 2(b)) that the pores of the as-prepared alumina membrane were well-defined, straight, with smooth inner surface. Fig. 2(c) shows the top image of FE-SEM of as-prepared AgI nanowires after partial removal of the porous alumina template, and Fig. 2(d and e) show the cross-sectional views of AgI nanowires after complete removal of the porous alumina membrane. These nanowires were individually separated from one another. The individual AgI nanowires were dense and continuous with a uniform diameter throughout their entire length. The diameter of the nanowires was approximately 70 nm, equal to the pore diameter of the alumina membrane. The surface of the nanowires was smooth due to the smooth inner wall of the alumina membrane. In short reaction times (0.5–2 h), only small segments of AgI were formed, but no nanotubes were observed

† Electronic supplementary information (ESI) available: FE-SEM images. See http://www.rsc.org/suppdata/cc/b3/b310212b/

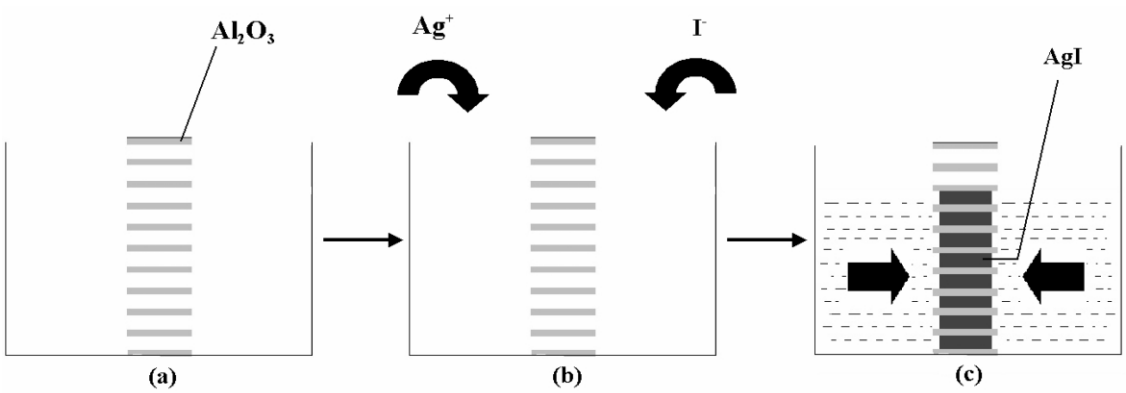

Fig. 1 Schematic diagram for the fabrication of AgI nanowires.

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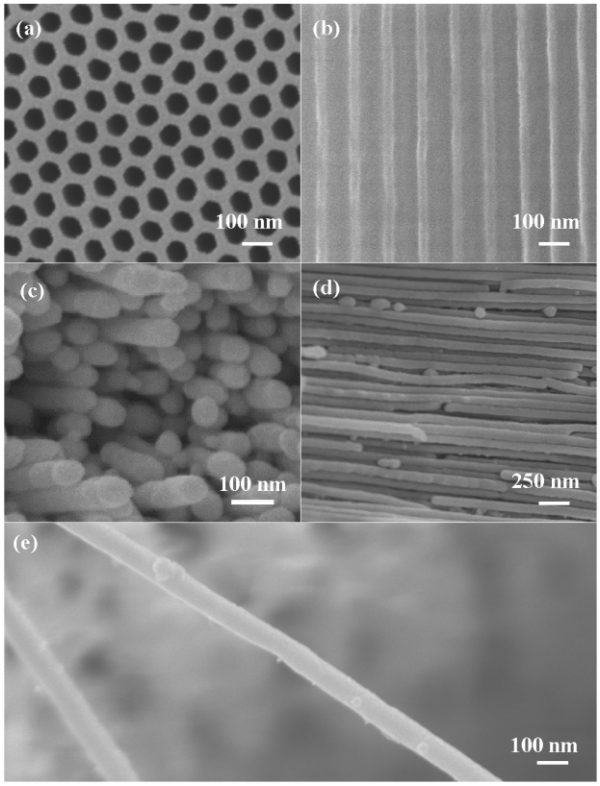

Fig. 2 FE-SEM images of the surface (a), the cross-sectional views (b) of the ordered porous alumina membrane, the top image of as-prepared AgI nanowires after partial removal of the porous alumina template (c), and the cross-sectional views of as-prepared AgI nanowires after complete removal of the porous alumina template (d and e).

under the present experimental conditions. The pore diameter and length of the porous alumina membrane could be easily controlled by varying adjustable parameters such as the anodizing voltage, anodizing time, temperature, and chemical treatment time. Thus, the diameters of the nanowires could be precisely controlled accordingly. We also prepared AgI nanowires of about 50 nm diameter (electronic supplementary information†).

The concentrations of $AgNO_3$ and KI aqueous solutions were varied from 0.01 M to 0.1 M. The FE-SEM images of as-prepared AgI nanowires at each of the concentration conditions showed no obvious differences.

The composition of as-prepared AgI nanowires was characterized by energy dispersive X-ray spectroscopy (EDX). The EDX spectroscopy indicated that only silver and iodine were present in the nanowires and that the ratio of silver to iodine atoms was 1 : 1 (Fig. 3.).

The structure of as-prepared AgI nanowires was also investigated by transmission electron microscopy (HR-TEM; Jeol JEM-3000F). Fig. 4 displays representative TEM images and electron diffraction pattern indicating the presence of the polycrystalline nature of AgI nanowires.

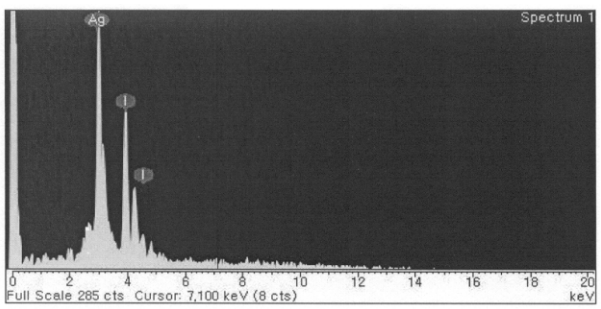

Fig. 3 Energy dispersive X-ray spectroscope of AgI nanowires.

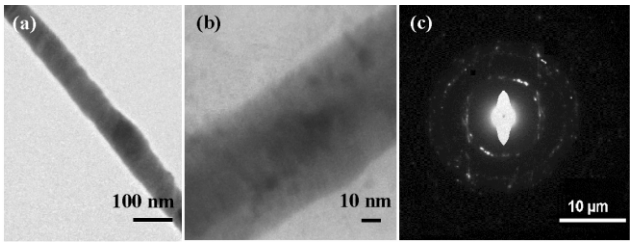

Fig. 4 Typical low-magnification (a) and high-magnification (b) TEM images of as-prepared AgI nanowires, and electron diffraction pattern (c).

In summary, we report the preparation of long and dense AgI nanowires using nano-sized porous alumina membrane templates. The process reported in this communication is very simple and easy to control. Since the procedure is not material-specific, a wide range of nano-sized inorganic materials could be prepared by this method. Further investigations on the conductive properties of as-prepared AgI nanowires are in progress.

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