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# Template route toward a novel nanostructured superionic conductor film; AgI nanorod/$\gamma$-$Al_2O_3$

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**A hierarchically structured composite ion conductor film (AgI nanorod/$\gamma$-$Al_2O_3$) was chemically prepared using nanoporous anodic aluminium oxide (AAO) as a template, where ion conducting AgI nanorods (av. diameter = 75 nm) are periodically aligned within a hexagonally organized insulating $Al_2O_3$ matrix.**

Composite solid electrolytes, where ion conducting solids (such as AgI, AgCl, AgBr, LiI, CuCl, *etc.*) are heterogeneously mixed with an insulating solid dispersant (such as $\gamma$-$Al_2O_3$, $SiO_2$, MgO, *etc.*), have attracted much research attention due to their markedly enhanced conductivity with respect to pristine ion conducting solids themselves.[1–3] Among many composite ion conductor systems, AgI/$\gamma$-$Al_2O_3$ composite solid electrolytes have been extensively studied and impedance measurements revealed a maximum conductivity enhancement by a factor of $10^3$–$10^4$, even at room temperature, compared with pristine $\beta$-AgI.[3] It is generally accepted that interface interactions between the ionic conductor (AgI) and insulator ($\gamma$-$Al_2O_3$) play a key role in governing the transport behaviour.[2] Although it has been suggested quite recently that such an enhanced conductivity is a consequence of the formation of an interfacial conducting phase (*e.g.*, 7H polytype of AgI with stacking fault arrangement), the microscopic mechanism or the origin of the enhancement in ionic conductivity is, as yet, not clear.[4] The interfacial interaction between particles could be maximized by reducing the size of particles down to 140 nm, since the surface of fine particles with high specific surface area are not only structurally unsaturated but also chemically labile and so can be easily converted to metastable phases. Previously, the fabrication of such composite ion conductors have been simply achieved by mechanically mixing and grinding the constituent materials (*i.e.* AgI and $\gamma$-$Al_2O_3$) and then hydrostatically pressing the resulting solid mixture, which does not, however, ensure homogeneous mixing of the components.[4,5]

Herein we report the synthesis and characterization of a hierarchically structured composite ion conductor film (AgI nanorod/$Al_2O_3$), where ion conducting AgI nanorods are homogeneously and periodically aligned within an insulating $Al_2O_3$ matrix with hexagonally organized configuration. A novel composite conductor was realized using porous anodic aluminium oxide (AAO) as a template, the structure of which is characterized by a closely packed regular array of hexagonal columnar cells with uniform nanoholes each of which contains a long cylindrical nanochannel.[6] The synthetic procedure for the preparation of the AgI nanorod/AAO composite is schematically presented in Fig. 1.

The nanoporous anodic aluminium oxide (AAO) template was prepared by a two-step anodization technique as described previously.[7] A field emission scanning electron microscopic (FE-SEM; Hitachi S-4300) image of the as-prepared AAO indicated that the template contained a well-organized hexagonal array of cylindrical pores with an average pore diameter of 75 nm and a pore density of 1 × $10^{10}$ $cm^{-2}$ (Fig. 2(a)). According to XRD (Philips PW3710) pattern of the as-prepared AAO, the nanoporous AAO turned out to be X-ray amorphous, showing a broad spectral feature over the $2\theta$ range 15–35°. However, the corresponding FT-IR (Bomem DA 8) spectrum showed a characteristic Al–O vibration of $\gamma$-$Al_2O_3$ with a shoulder at *ca.* 1180 $cm^{-1}$ and strong absorption bands at 600–900 $cm^{-1}$.[8]

The Ag nanorod/AAO composites were fabricated *via* the electrodeposition of silver within the pores of the alumina template. A through-hole AAO membrane was used in the preparation of the Ag nanorod array. Initially, a layer (*ca.* 120 nm thick) of Ag was thermally evaporated onto one side of membrane to make the surface electrically conductive. This

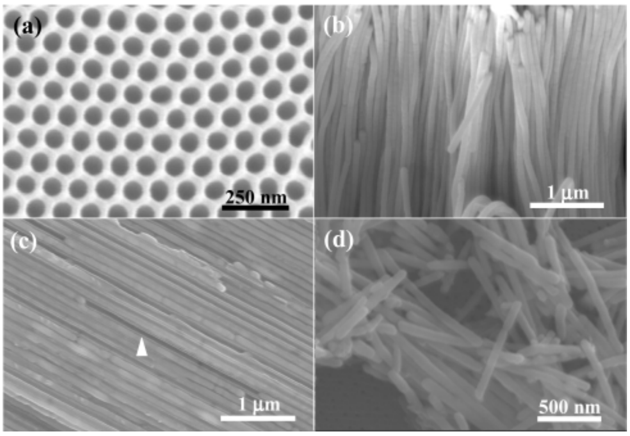

**Fig. 2** FE-SEM images of (a) AAO template, (b) Ag nanorods after removing the AAO template, (c) cross-sectional image of AgI nanorod/AAO, and (d) AgI nanorods after removing the AAO template.

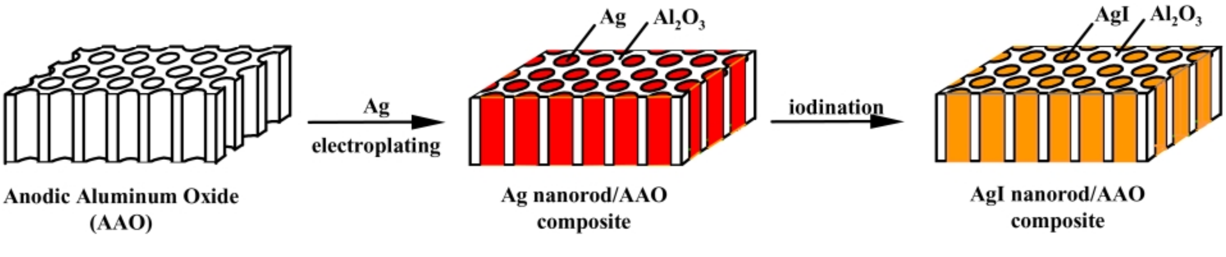

**Fig. 1** Scheme for the fabrication of the AgI nanorod/AAO composite.

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conducting layer functions as the working electrode in the electrodeposition of silver. After this, Ag was electroplated using a commercial plating solution (Technic silver 1025A and B) at room temperature. Electrodeposition of silver on the nanoporous AAO membrane produced large arrays of silver nanowires with a uniform diameter and a very large aspect ratio. As evidenced by FE-SEM investigation, the average diameter of the resulting metal nanowires is highly consistent with the average pore diameter (75 nm) of the alumina template used in the electrodeposition (Fig. 2(b)).

Fabrication of the silver iodide nanorod array was readily achieved by utilizing the solid–gas reaction between metallic silver nanorods and gaseous iodine. This reaction is known as iodization or iodination of silver;[9] a typical metal oxidation process where iodine serves as an oxidant. The net reaction can be expressed by eqn. (1):

$$2\ \mathrm{Ag(s)} + \mathrm{I_2(g)} \rightarrow 2\ \mathrm{AgI(s)} \qquad (1)$$

Typically, iodination was carried out by heating a vacuum sealed Pyrex tube containing 2 g of elemental iodine and a piece ($0.5 \times 1$ cm$^2$) of Ag nanorod/AAO composite film in a constant temperature furnace (150 °C) for 24 h. After completion of the reaction, the resulting AgI nanorod/AAO composite was isolated after subliming the excess iodine, thoroughly washing with acetone and water to remove the residual elemental iodine, and finally drying under vacuum.

A representative cross-sectional FE-SEM image of the AgI nanorod/AAO is shown in Fig. 2(c). Some of the nanochannels (white triangle marks in Fig. 2(c)) of AAO were not filled with AgI nanorods probably due to the mechanical force applied to the film in order to obtain the cross-sectional image of the AgI nanorod/AAO composite film. An FE-SEM image of AgI nanorods freed from alumina by dissolving the oxide matrix with 0.5 M NaOH solution is shown in Fig. 2(d). Unlike the image of Ag nanorods in Fig. 2(b), the direction of the rod axis of individual AgI nanorods is rather arbitrary and the length of each nanorod is relatively short. Such morphological evolution can be attributed to the brittle nature of ionic AgI nanorods compared to metallic Ag nanorods and to the external stress exerted during the processes of eliminating the alumina matrix and drying the resulting AgI nanorods. Each of AgI nanorods in the nanochannels of the AAO matrix, however, is expected to have a high aspect ratio aligning its rod axis perfectly orthogonally with respect to the surface of AAO.

The phase of the synthesized nanorods was checked by TEM and X-ray diffraction (XRD). A selected area electron diffraction (SAED) pattern of the present AgI nanorods indicated that the sample is polycrystalline showing diffuse ring patterns. According to the estimated lattice spacings from the diffraction rings, the sample is mainly composed of a hexagonal wurtzite type β-AgI and this assignment was confirmed by XRD. Typical XRD spectra of Ag nanorod/AAO and AgI nanorod/AAO composites are presented in Fig. 3, together with the spectrum of commercial AgI for comparison. Broad spectral features in the $2\theta$ range 15–35° were observed for the Ag nanorod/AAO and AgI nanorod/AAO composite samples, which originated from amorphous alumina ($Al_2O_3$). The XRD spectrum of the Ag nanowire/AAO composite showed well defined (111), (200) and (220) lines at $2\theta = 38.8$, 44.1 and 64.7°, respectively, revealing pure metallic silver (JCPDS code # 03-0931). On the other hand, it is evident from the present XRD patterns that the iodination reaction on the Ag nanorod/AAO composite gives rise to significant changes in the diffraction patterns. According to our XRD analysis, the observed diffraction peaks in the AgI nanorod/AAO composite could be indexed to the β-AgI structure with lattice parameters $a = 4.6$ Å and $c = 7.5$ Å (JCPDS code # 09-0374), consistent with the analytical result of the SAED pattern.

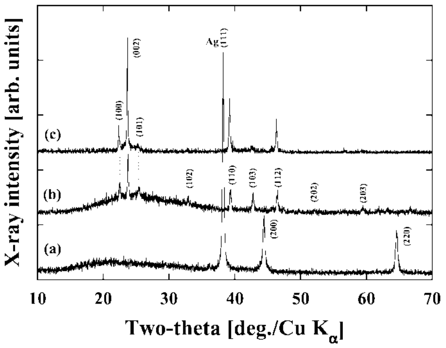

**Fig. 3** Cu-Kα powder X-ray diffraction (XRD) pattern of (a) Ag nanorod/AAO, (b) AgI nanorod/AAO composite film, and (c) commercially available AgI.

Our preliminary results on ionic conductivity measurements revealed that the present AgI nanorod/AAO composite showed a three orders of magnitude enhanced ionic conductivity ($\sigma_{(28\,°\mathrm{C})} = (1.67 \pm 0.03) \times 10^{-3}\ \Omega^{-1}\ \mathrm{cm}^{-1}$) compared with pristine β-AgI, which is comparable with the previously reported maximum values in physically prepared AgI/$Al_2O_3$ composite ion conductors.[3]

It has been pointed out that the interfacial effect together with size and texture are responsible for conductivity enhancement in composite ion conductors. Unlike the inhomogeneous structure of physically prepared conventional composite ion conductors, the present sample has a novel geometric structure, where ion conducting nanorods with high aspect ratio are periodically embedded in the nanochannels of porous anodic aluminium oxide (AAO). Moreover, the interfaces formed by the AgI nanorods and the walls of cylindrical nanochannels of AAO are expected to act as well defined, isolated, and discrete conduction channels, leading to a markedly enhanced ionic conductivity. Therefore, the present AgI nanorods/AAO composite film might provide a good model system for elucidating the origin of the conductivity enhancement as well as the mechanism governing the transport behaviour in composite conductors.

We are quite certain that our underlying concept to develop novel nanostructured composite ion conductors can be readily extended to other solid electrolyte systems such as LiI and CuCl. We are at present investigating the transport properties of the present composite conductor with variation of the physical dimensions of the AgI nanorods, such as rod diameter and length.

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