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PREPARATION AND CHARACTERIZATION OF Ag_2Se NANOWALLED TUBULES BY ELECTROCHEMICAL METHOD

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In this paper, we report the preparation of nanowalled hollow tubules of Ag_2Se in to the pores of track-etch membrane (TEMs). Using the electrolyte solution (0.01 M $AgNO_3$ and 0.3 M SeO_2 + 0.03 M H_2SO_4 + 50% DMSO), a current density 0.06 A cm^{-2} was applied for 20 minutes. The tubules were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD) and energy dispersive X-ray (EDX) techniques. The SEM photographs show the high aspect ratio of the tubules and EDX analysis shows good stiochiometric composition of the Ag_2Se product.

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1. Introduction

Hollow nanostructures due to their special characteristics such as large surface to volume ratio, low coefficient of thermal expansion and low density attract much attention of scientist community in the past few years. Hollow structures also have potential applications in antireflection surface coatings, catalysis and rechargeable batteries [1-2]. The biomedical applications of hollow nanotubules such as drug delivery, cell imagining and sensing of biomolecules have been reported by several authors [3-4]. Their capacity for encapsulating sensitive materials such as therapeutics, fluorescent markers and field responsive agents have been exploited by many groups for drug delivery and biomedical imaging [5-6]. Hollow SnO_2 nanosphere shows high initial reversible charge capacity and improved cyclic performance as compared to SnO_2 nanoparticles [7]. It has been reported that Pt hollow nanosphere shows enhanced catalytic activity for methanol oxidation of solid pt nanosphere with roughly the same size [8].

The progress in fabrication of hollow structures has provided great opportunity for their wide application in many current and emerging areas of industry and technology. Many authors have reported the template-free method for synthesis of hollow particles which has no control over the size and shape of the particles [9]. The template based synthesis of hollow sphere of Au and Ag with silica also reported [10]. But the survey of the literature shows that very limited methods are present for producing uniform hollow high aspect ratio nanotubules. Here we present the template based method for fabrication of high aspect ratio hollow structures which has complete control over size shape and chemistry. By this method we have synthesized the Ag2Se hollow tubules. Ag_2Se, an important I-IV ($A_2^{I}B^{IV}$) group compound semiconductor has potential

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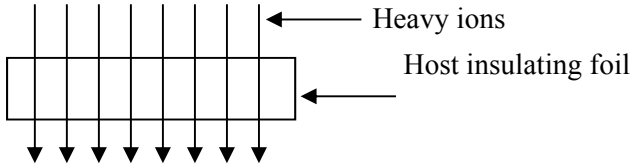
applications in solid electrolyte in photochargable secondary batteries [11-13]. The electrochemical performance of Ag_2Se based photochargable secondary battery may be improved by using the high aspect ratio hollow tubules. The large surface to volume ratio of the hollow tubules may provide extra space for the storage of ions, which leads to the enhancement of specific capacity of the batteries. This ratio of hollow nanotubules reduced effective diffusions distance for ions and hence provides better rate capabilities.

Keeping in mind the above wide future applications of hollow structures, we report here the synthesis of Ag_2Se nanowalled high aspect ratio hollow tubules using TEMs as template. The tubules of Ag_2Se have been prepared by simple electrochemical deposition using two electrode chemical cell. Electron microscopy, XRD and EDX characterization were performed for morphological, structural and qualitative analysis respectively.

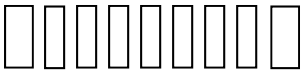
2. Experimental

Polycarbonate (PC) Makrofol KG foils of thickness 15 μm were irradiated with Ag^{+13} ions (180 MeV) having flux of $10^7/cm^2$ utilizing the heavy ion accelerator facility at Inter University Accelerator Centre (IUAC), New Delhi. Samples were etched in 6 NaOH solution at 60^0 C. Production of stable hollow nanowalled tubules by electrodeposition using TEM as a template is illustrated in following steps of figure 1.

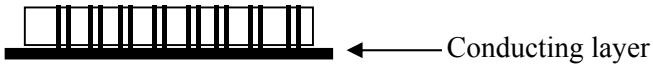
(a) Production of Latent tracks by heavy ions
(b) Chemical amplification of latent tracks.
(c) Deposition of a conducting layer on one face of the membrane and electrochemical filling of the pores
(c) Dissolution of the host membrane in suitable solvent, resulting in array of Tubules



a) Production of latent tracks by heavy ions



b) Chemical amplification of Latent tracks



c) Deposition of a conducting layer on one face of the membrane and electrochemical filling of the pores

d) Dissolution of the host membrane in suitable solvent, resulting in array of microtubules

Fig. 1. Schematic diagram of tubule formation by template synthesis

Uniform cylindrical pores were obtained in PC membrane by controlled etching [14]. The cathode of the cell was covered with the etched PC membrane and the electrolyte (0.01 M $AgNO_3$

and 0.3 M SeO_2 + 0.03 M H_2SO_4 + 50% DMSO) was used. A current density 0.06 A cm^{-2} was applied for 20 minutes. For generating the hollow tubule, the process was interrupted before the pores were completely filled which led to material deposition layer by layer on the pore walls. For synthesis of hollow tubules with the basic knowledge of electrochemistry, the conditions for good electrodeposition were optimized by various experiments and trials. The finally processed sample was dissolved in CH_2Cl_2. The cleaned and dried samples were mounted on special designed aluminum stubs with the help of the two way adhesive tape, coated with a layer of gold using JEOL, FINE SPUTTER JFC-1100 sputter coater and viewed under JEOL, JSM 6100 SEM. The crystallographic studied were carried out using Philip 1710 x-ray diffractometer in 2θ range from 10^0 to 70^0 using CuKα radiation. EDX analysis of nanotubules was carried out by RENTEC: Model QX-1 instrument.

3. Results and discussion

The proposed mechanism of formation of Ag_2Se hollow tubules by electrodeposition in two electrode electrochemical cell is as follows

In the presence of slight H_2SO_4, the $AgNO_3$ aqueous solution dissociates as

$$AgNO_3 \longrightarrow Ag^+ + NO^-_3$$

Now the produced silver ions catalyze the disproportional process of Se^0 into Se^{2-} and Se^{4+}. Due to the versatility in the oxidation states of Se i.e. Se^0, Se^{2-}, Se^{4+} and Se^{6+}, the cathode reaction of Ag_2Se follows a complex mechanism.

The Se^{2-} species combined with Ag^+ ions to generate Ag_2Se product as

$$2\,Ag^+ + Se^{2-} \longrightarrow Ag_2Se$$

Than the Se^{4+} diffuse out of the solid matrix and react with Ag^+ and H_2O to form Ag_2SeO_3 in the aqueous medium in the pores of template.

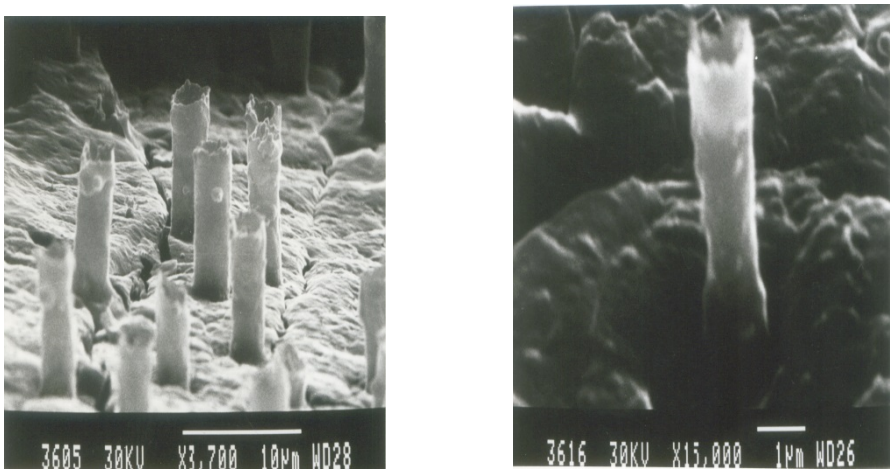
$$2\,Ag^+ + 3\,H_2O + Se^{4+} \longrightarrow Ag_2SeO_3 + 6\,H^+$$

So, overall reaction can be presented as

$$6\,Ag^+ + 3\,Se + 3\,H_2O \longrightarrow 2\,Ag_2Se + Ag_2SeO_3 + 6\,H^+$$

The solid byproduct Ag_2SeO_3 formed is out of the solid matrix can be easily removed by washing the product with hot water.

In fig. 2 (a, b), the shape of the tubules directly reflects the geometry of the pores in TEMs. There is clear evidence that under the employed irradiation and etching conditions, the pores are well aligned and have cylindrical geometry. The surface smoothness of the tubules depends on several factors such as quality of polymer and etching conditions. A speculative explanation for the mechanism responsible for tubule formation using template synthesis is shown in schematic diagram (figure 3). The walls of the membrane (PC) used are anionic (time t = 0) and electrostatic attraction contribute to the absorption of the nascent material into the walls of the pores (time t_1). Obviously, the deposition along the pore walls continues until the pores are completely blocked. Finally, in order to allow the formation of the tubules, the process has to be interrupted at an optimum time depending upon the experimental conditions. The gas formation during electrodeposition process is helpful in tubule formation because pores may provide an exit passage or outlet for the gas, which would push the material to be deposited towards the pore walls (time t_2). The presence of air bubbles and evolution of hydrogen during deposition at too high voltage affects the quality of the tubules.



(a) (b)

Fig. 2 (a,b). SEM photographs of high aspect ratio Ag_2Se nanotubules

In the beginning walls of the pore are anionic (t = 0).The electrostatic attraction contributes to the deposition of the Ag_2Se into the walls of the pores (time t_1). The gas would push the material to be deposited towards the pore walls (time t_2).

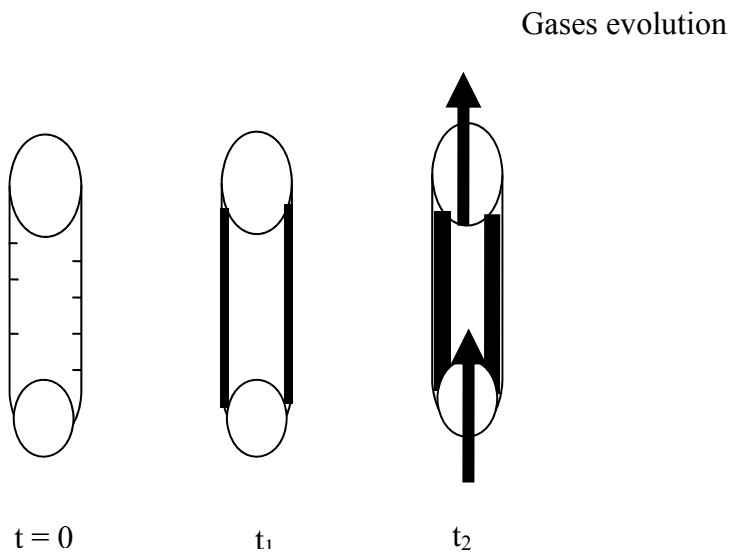


Fig. 3. Tubule formation mechanisms

The figure 4 displays the XRD pattern, which shows that structures are single phase orthorhombic as already reported in literature [15]. The sharp diffraction peaks shows the good crystalline nature of the hollow tubules.

The result of EDX spectrum (figure 5) shows that atomic ratio of these hollow tubules is 61.05 : 38.95, very close to the stiochiometric composition of the Ag_2Se. The high aspect ratio and large surface to volume ratio of the hollow tubules may beneficiary in enhancing the specific capacity of the batteries. As the tubules are well separated from each other, the distance between

the tubules overcome the problem of pulverization and aggregation of the electrode materials leads to improve the cyclic performance of the batteries.

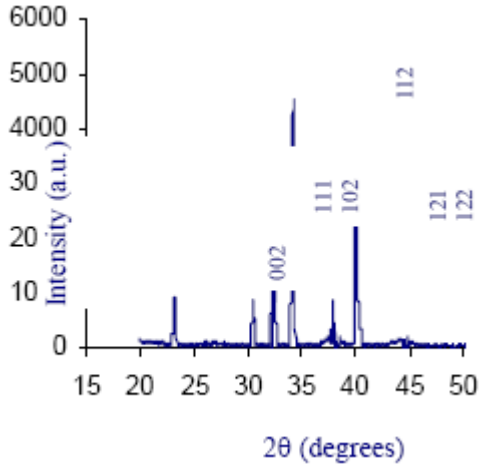


Fig. 4. XRD pattern of Ag_2Se hollow tubules

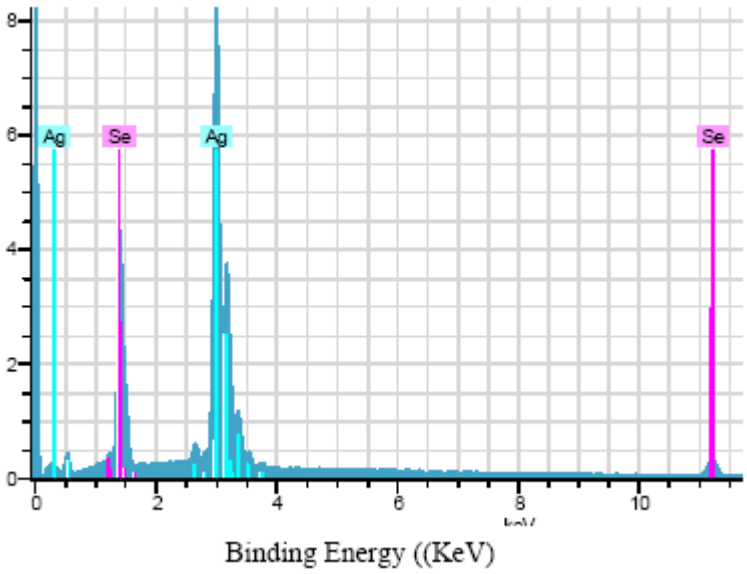


Fig. 5. EDX spectrum of Ag_2Se hollow tubules

Table 1: EDX results of the sample showing elements, atomic number, series, weight % and atomic % of the elements

Elements	Atomic Number	Series	Weight %	Atomic %	Error %
Ag	47	L-series	68.17	61.05	2.2
Se	34	K-series	31.83	38.95	1.1

4. Conclusions

In summary the template based synthesis is an effective rout to produce hollow structures of Ag_2Se at room temperature. The SEM analysis shows that tubules have high aspect ratio and uniform in diameter. The XRD pattern shows that structures are single phase orthorhombic and sharp diffraction peaks indicate the good crystalline nature of the hollow tubules. The EDX analysis confirms the good stochiometry ratio of Ag and Se. In future, these high aspect ratio hollow tubules may be used to increase active area of catalysis, energy storage, and drug delivery system. These hollow tubules due to their high surface to volume ratio, act as good candidates for cathode in batteries and hence may increase the electrochemical performance of Ag_2Se based photochargable secondary batteries.

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