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Electrochemical synthesis of copper nanotubules in etched ion tracks in polycarbonate

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There is a tremendous increase in research in the area of nanoscale materials because of their expected unique physical properties (e.g., optical, electronic, magnetic, etc.) and also because of wide ranging applications in various areas including physics, chemistry, electronics, optics, biomedical sciences and materials sciences [1–10]. In material science, the fundamental interest is in the physical properties of a material can change in the transition between the bulk scale and the nano scale. There are several methods for the preparation of nanoscale materials such as molecular beam epitaxy, nanolithography, etc. However such nanoscale materials can also be fabricated using a different method known as template synthesis. In this method, thin fibrils of the desired material are electrochemically synthesized within the pores of the template material. Interestingly, depending on the nature of the material and on factors such as the chemistry of the pore wall, this cylindrical fibrils may be solid (a nanowire) or hollow (a nanotubule) [3–7]. Though there exists a wide range of nanoporous materials, most studies have been performed using track-etched polymer membranes and anodic alumina membranes [1–4]. The major difference between the lithographical defined templates and the other artificial template membranes mentioned above is a much shorter aspect ratio in the former.

A variety of fibrils of metals and conducting polymers can be electrochemically produced within the pores. After the dissolution of the membrane, the wires can be freed from the membrane, collected and then observed using electron microscopy. Such observation offers a powerful characterization tool for membranes as it gives information about the inside of the membrane: thus, the shape of the pore and its size can be determined. For the formation of suitable ion track membranes, the track etch rate (V_t) should be much larger than the bulk etch rate (V_b). The ratio V_t/V_b determines the resulting geometry of the pores. In particular, polycarbonate have been used in the membrane technology because of high V_t/V_b ratio for several hundreds to 1000 leading to extremely cylindrical pores. In the present work we report the synthesis of copper nanotubules in etched ion tracks in polycarbonate. The morphology and crystallinity of the copper nanotubules were studied by means of scanning electron microscopy (SEM) and X-ray diffraction.

10 μm thick foils of polycarbonate were irradiated with heavy ions ^{238}U (11.6 MeV/n) at normal incidence utilizing the UNILAC facility at GSI, Darmstadt, Germany. The fluence was 10^6 ions/cm^2. Using these conditions, the penetration range of the ions in polycarbonate was larger than the thickness of the foils and the dE/dx of the ions was well above the threshold required for homogeneous etching. The irradiated polycarbonate foils were etched chemically at 60 °C in a 6N NaOH solution containing 10% methanol for 5 min. The resulting pores are cylindrical, their diameters increase linearly with time of etching. In the present work we created the pores with diameter 400 nm.

In general, a suitable cell design is required and the lay-out design of such a cell along with other relevant details of the technique has been discussed previously [3]. Two electrode electrochemical cell was used for copper deposition in the pores of the template. A solution of 200 g/l $CuSO_4 \cdot 5H_2O$ and 20 g/l H_2SO_4 in Milli Q 18 MΩ water. The pH of the solution used was adjusted to 0.90. The electrodeposition was carried out for 6 min at 0.56 V (0.0112A to 0.0136A). A high

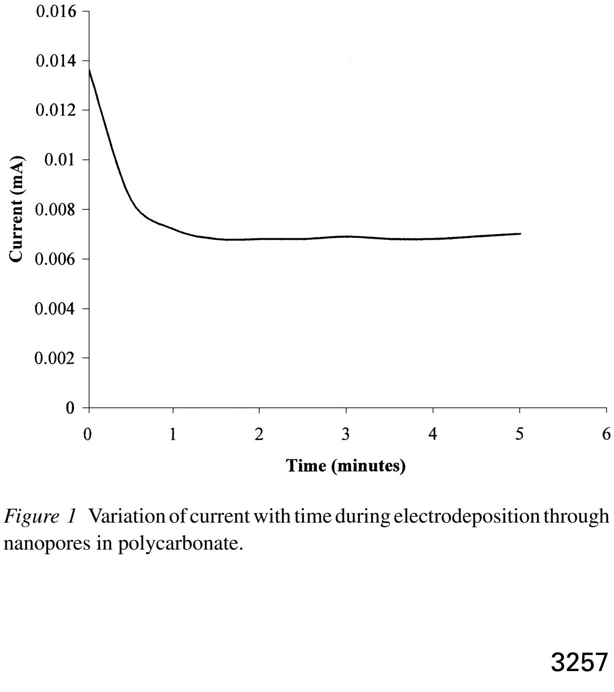

Figure 1 Variation of current with time during electrodeposition through nanopores in polycarbonate.

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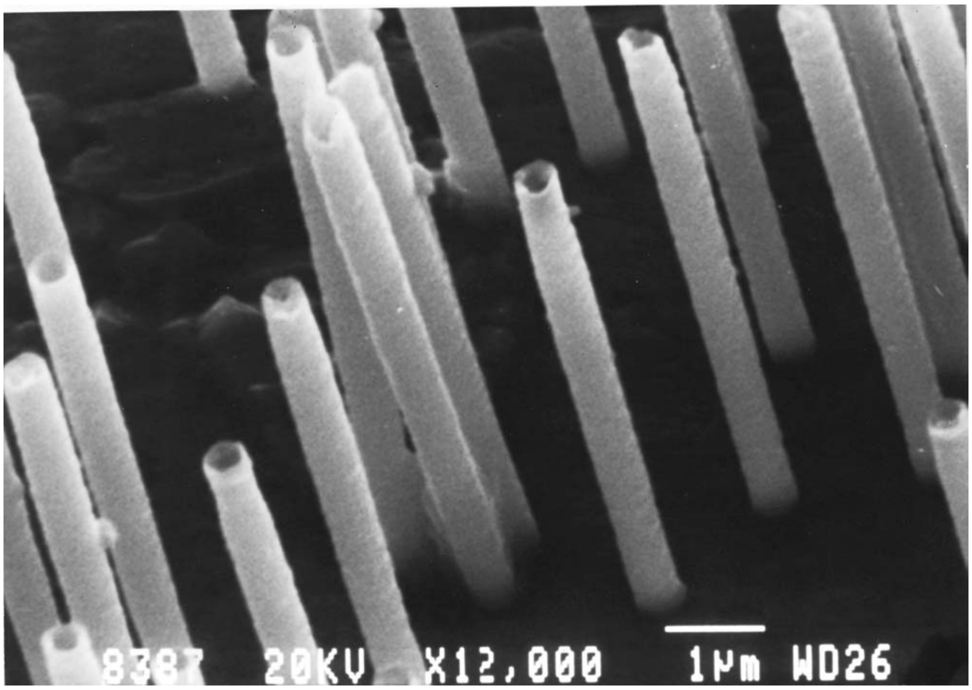

Figure 2 SEM microphotograph of copper nanotubules having diamater 400 nm and length 3.5 μm.

concentration of $CuSO_4$ is important to provide a sufficiently large number of copper ions inside the pores during the galvanic deposition process. Sulfuric acid increases the conductivity of the solution and lowers the cathode overvoltage. Electrodeposition was performed potentiostatically at room temperature i.e., 30 °C. By applying low voltage, side reactions such as hydrogen evolution were avoided. During the deposition process, we recorded the electrical current as a function of time (Fig. 1). After the electrodeposition was over, the electrolyte was drained out and the cathode flushed with 3% H_2SO_4, followed by Milli Q Water rinsing and air-drying.

For the characterization of the tubules by means of SEM, copper tubules, freestanding on the copper tape, were observed by dissolving the polycarbonate matrix in dicholoromethane. The cleaned and dried samples were mounted on the specially designed aluminum stubs with the help of double adhesive tape, coated with a layer of gold palladium alloy in Jeol, Fine Sputter JFC 1100 sputter, coated and viewed under Jeol, JSM 6100 scanning microscope at an accelerating voltage of 20 KV. Images were recorded on the photographic film in the form of negatives at different magnifications. The metallic nanotubules having diameter of the order of 400 nm with stochastically distributed elements revealing the finer details of the constituents and of the etched pores of the host NTF are shown in Fig. 2.

In order to confirm the crystalline quality, X-ray diffraction was performed on tubules of diameter 400 nm. X-ray diffraction measurements were carried out using a Philips PW1710 diffractometer with Cu-K_α radiation in 2θ mode. The diffractogram of the sample shows four peaks confirming the poly crystalline nature of nanotubules. Measured intensities for the (111), (200) and (220) reflections are much smaller than expected for a standard powder sample (Fig. 3).

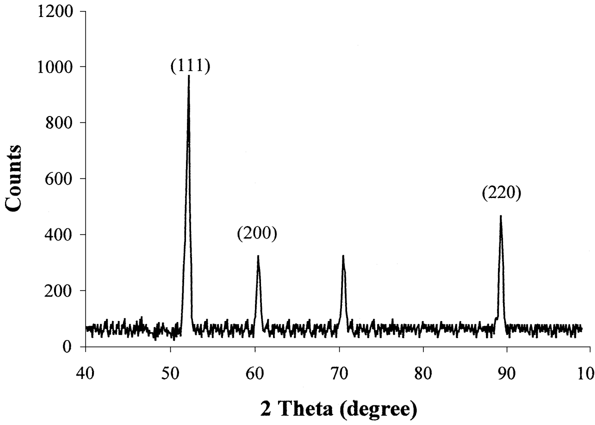

Figure 3 XRD diffractogram for the electrodeposited Cu nanotubules having a diameter of 400 nm.

A speculative explanation for the mechanism responsible for tubule formation in the template synthesis of organic micro/nanotubules is that if the walls of the membrane/filter used are anionic for example in the case of (polycarbonate), the electrostatic attraction may contribute to the absorption of the nascent material into the walls of the pores [8, 9]. Furthermore in the case of metallic tubules, the growth proceeds if the pore walls provide molecular anchors which help the guest material to form a thin skin which lines the pore walls. In the present work ion track membrane was dipped in 0.05 M $SnCl_2$ solution for 3 min for providing molecular anchors to the pore walls. Obviously, the deposition along the pore walls continues until the pores are totally blocked. Finally in order to allow the formation of the tubules, the process has to be terminated at an optimum time depending upon the experimental conditions and the tubule size requirements. Gas formation during electrodeposition processes is helpful in tubule formation. The pores may provide an exit passage or outlet for the gas which would push the material to be deposited towards the pore walls helping the molecular anchors to be more effective. An interesting possible application of these nanotubules may lie in their use as an alternative to electron impact ion sources—the volcano field ion sources. Further studies related to possible applications of these copper nanotubules are being made.

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