Short communication

Potassium hydrogen phthalate (KAP) micro- and nano-rods prepared by a template approach

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Micro and nanorods of potassium acid phthalate (KAP) with diameters ranging from a hundred nanometers to tens of microns were obtained by solution growth in polycarbonate (PC) ion track templates. The ion track templates were produced by swift heavy ion irradiation of PC foils (e.g. U with 11.4 MeV/nucleon specific energy) and subsequently etching. After the growth the host templates were partially dissolved in dichlormethane and imagined by scanning electron microscopy. The template approach allows the fabrication of arrays of uniform nanostructures with a controlled morphology.

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1. Introduction

The template approach provides a simple method to produce complex and functional nanostructures with controlled morphology. Despite the fact that template synthesis has been applied over decades to a broad range of problems in nanoscale electronics, bioanalytical chemistry, magnetic materials, energy conversion, and other areas, some of the new developments in the field are quite surprising and unanticipated. This suggests that much remains to be discovered by using this method.

There is a wide variety of areas, including optoelectronics, data storage, and sensing for the potential applications of nanorods, nanotubes or nanowires arrays [1]. Having a radius ranking from few nanometers to a few hundreds of nanometers, these nano-structures exhibit unique properties relative to bulk structures due to their small size, which leads to large surface-to-volume ratios and size-dependent effects. For our studies we use the template approach which consists in filling the pores of an etched ion track membrane, prepared by heavy ion irradiation and chemical etching, with the desired material by different methods [2-8].

In this paper we use the crystallization process from solution for filling the etched track polymers templates in order to obtain potassium acid phthalate (KAP) nanorods. The solution crystallization method which we employ in the present study was already used for the growth of KI micro and nanorods [9] and KCl or NaCl cylindrical nanorods [10]. Potassium hydrogen phthalate or potassium acid phthalate is a material very soluble in water and crystallizes in normal conditions. Recent papers showed extremely interesting properties of dye doped single crystals such as potassium acid phthalate [11]. In the present approach some problems related to the fabrication of dye doped materials for lasing media can be overcome. The most important feature of single crystals host materials is their high optical quality. Therefore, KAP nanorods growth behavior and their morphology was chosen as a model in this investigation for future studies on oriented growth of nanorods and nanowires. The morphological properties of the nano and micro rods were investigated using scanning electron microscopy.

2. Experimental

The template approach represents a promising method for fabricating nanosized objects with given geometrical properties. Thus, by using polymer nanoporous membranes one can fabricate not only cylindrical but conical or double-conical nanorods, taking into account that these nano-objects represent perfect replica of the hosting templates pores.

Foils 100 and 30 micrometers thick of polycarbonate were irradiated with swift heavy ions with the specific energy of 11.4 MeV/nucleon at the UNILAC linear accelerator (GSI Darmstadt). The fluences employed were in the range $10^5 – 10^8$ ions/cm^2.

Membrane etching was performed using chemical solutions with high selectivity. In removing by chemical etching of the ion track and nanopore formation there are two important parameters that are strongly influencing the shape and size of the nanopores. These are the etch rate along the ion track (track etch rate $–v_t$) and the etching rate of the non-irradiated bulk material (bulk etch rate – v_b). Any etched pore presents a conical shape in the case of exposing to the etching solution from one side or a double cone shape in the case of exposing to the etching solution from both sides (e.g. by completely immersing the foil into the etching solution). In the case of high selectivity etching ($v_t >> v_b$) cylindrical pores are obtained.

Aqueous solutions of 5 M NaOH containing 10% methanol or 6 M NaOH were use for etching the ion tracks at 50°C. This resulted in micro and nanoporous membranes containing cylindrical pores with a surface density corresponding to the ion fluence (i.e. for each ion track one pore is obtained) and with different diameters, depending on the etching time.

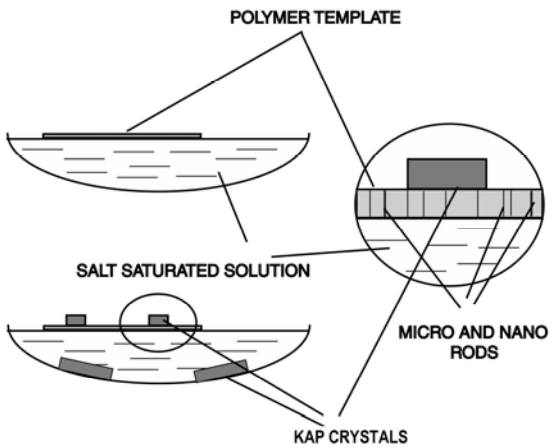


Fig. 1. Experimental arrangement employed for solution growth of crystalline nano and micro rods.

The growth of nanorods was performed from solution. A large number of parameters must be optimised in order to obtain nanowires with high morphological and structural quality. In Fig. 1 the experimental set-up used for obtaining KAP nanorods using the template method is presented. Thus, the polymer membranes were placed on the surface of a vessel containing a solution close to saturation. By slow evaporation of the solvent the saturation threshold is reached and crystallites start to grow both inside the solution and in membranes pores. Due to the restricted geometry of the nano and micro pores the rods growing inside are single crystals for the case in which the growth takes place sufficiently slow.

The membranes were removed from the solution after several days and left to dry on filter paper. The observation of the morphology was performed, after partial removing of the growth template by dissolving it in dichloromethane. Scanning electron microscopy was used to study the morphology.

3. Results and discussion

After removing the membranes from the growing solution, on their upper surface one can observe macroscopic crystals of KAP. These small crystals have grown on top of the micro- or nanorods grew inside the polymer membrane and their appearance indicates a tendency of a monocrystalline growth process.

The scanning electron microscope image presented in Fig. 2 shows a KAP crystal grown on the surface of a porous membrane, on top of the KAP nanorods.

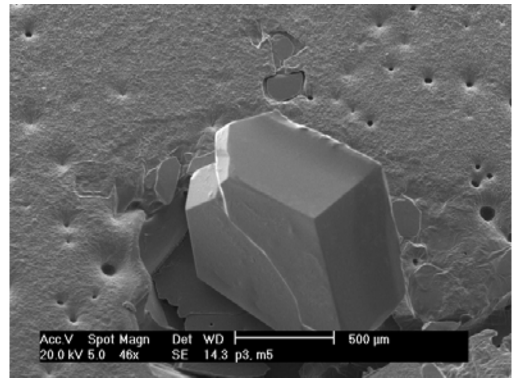
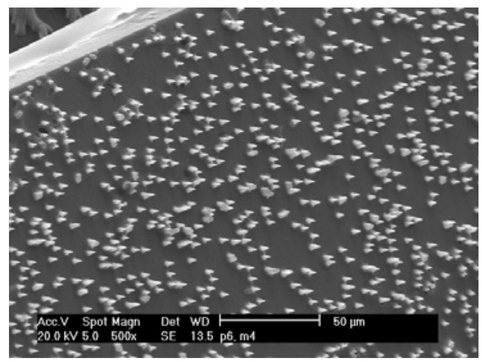


Fig. 2. KAP crystals grown from solution on the surface of a porous membrane.



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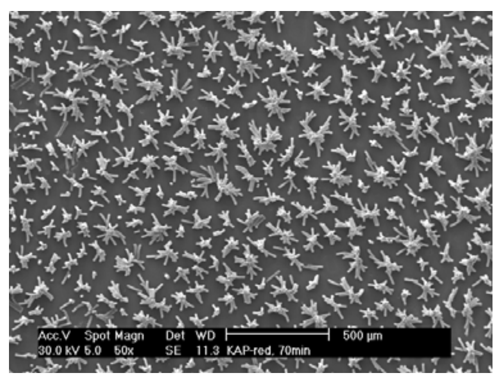

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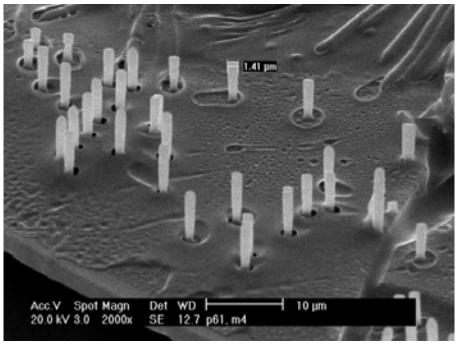
Fig. 3. Arrays of potassium hydrogen phthalate rods grown from solution a). partially dissolved membrane; b) totally dissolved membrane.

The same growth process takes place inside the pores of the membrane. In Fig. 3a it is presented the image of an array of KAP rod tips obtained after dissolving only a small layer from the surface of the polymer membrane. The rods of micrometer size show plastic properties. In Figure 3b it can be observed that during the dissolving of the polymer matrix the rods can be mechanically bent. This bending can be avoided if the membrane is only partially dissolved, as it can be observed in Fig. 4.



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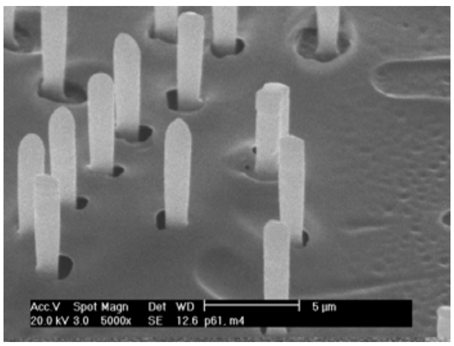

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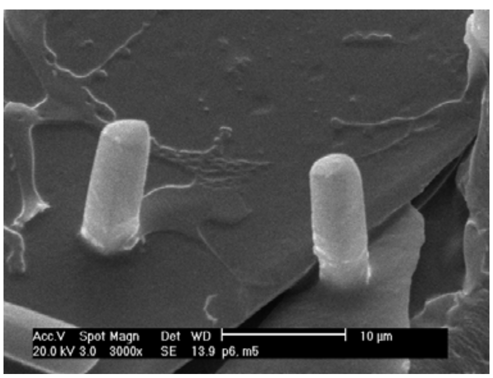
Fig. 4. SEM images of a partially dissolved membrane in which an array of potassium hydrogen phthalate rods was grown.



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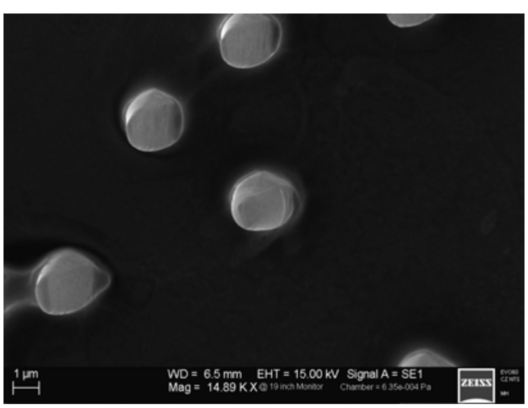

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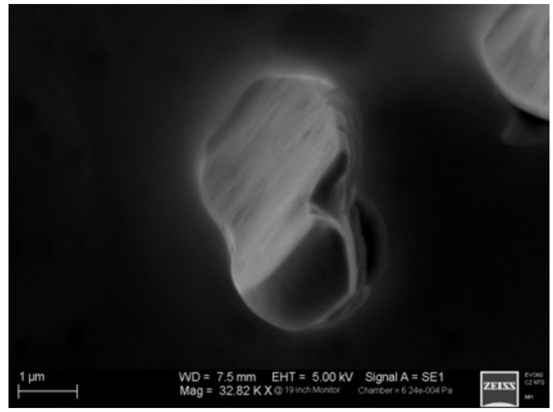

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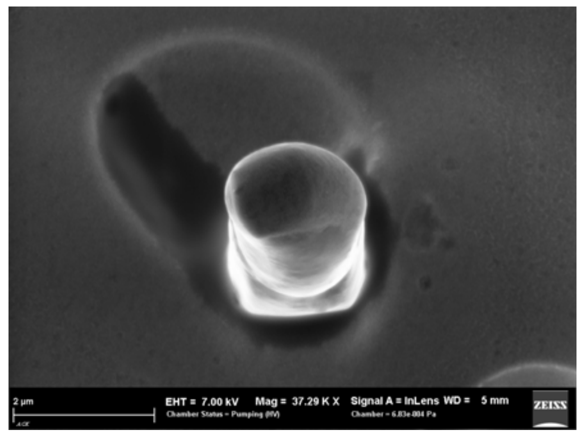

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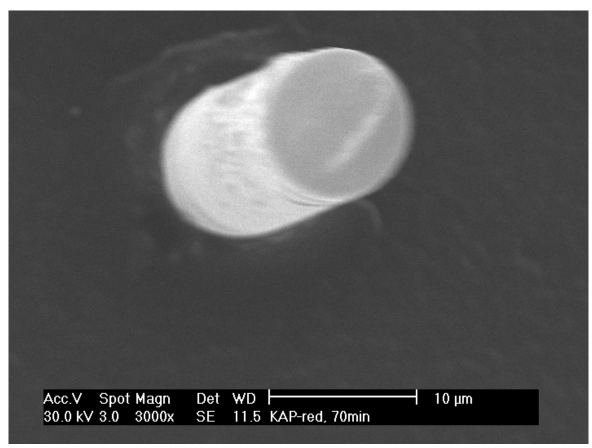

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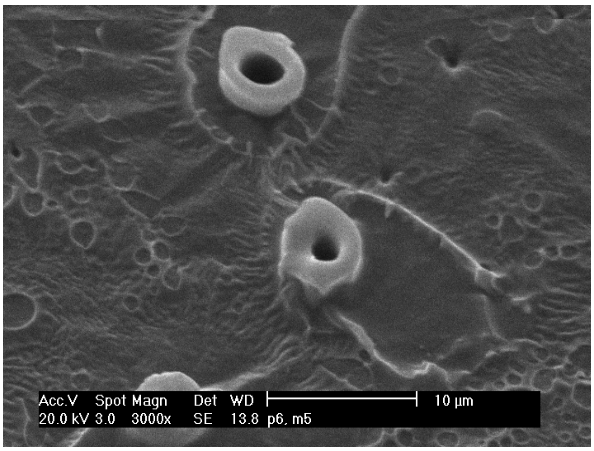
Fig. 5 . SEM images of the KAP nanorods presenting facets that show single crystal growth tendency for restricted pore geometry.

Because of the restricted geometry of the pores, for such materials where the single crystal growth tendency is high, we expect to obtain also single crystal rods inside the material. Indeed, we observed facets for the microstructural configurations, which are a clear indication of high ordered growth (Fig. 5). The growing process is very sensitive to factors such as evaporation rate or temperature that can alter the quality of the rods crystalinity. Thus, in Figure 5d can be observed how the structure of the rod changes during growth, the lower part of the rod presenting a clear square section while the upper part maintains the round section of the geometry of the pore.

Earlier, Dobrev and coworkers [5] observed some interesting phenomena for KI rods that were observed also in this case. Thus, hollow structures were formed in some cases due to the morphological instabilities of the growth, while for some of the structures bending occurs after dissolving the template (Fig. 6).



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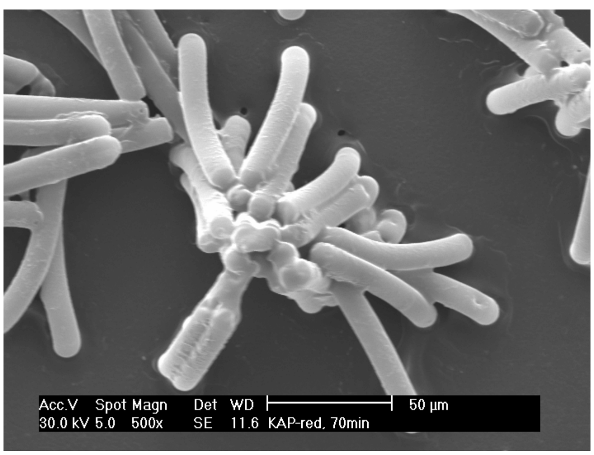

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Fig.6. (a) Hollow KAP rods; (b) microrod array where bended KAP structures can be observed.

4. Conclusions

The template method is a versatile approach in preparing highly uniform micro and nanostructures. The method was usually employed in performing electrochemical growth of micro and nanowires of metals and semiconductors. We applied solution growth to fabricate micro and nanorods of potassium hydrogen phthalate (KAP). Such structures have high potential for applications one example is the possibility to fabricate micro and nano lasers as it was recently proven for ZnO nanowires [12].

The growth process shows a strong tendency towards single crystalline structures. In some cases tubes were obtained. The behaviour of such microscopical objects, with high aspect ratio is in some cases different when compared to the case of bulk crystals. As an example bended rods were observed after dissolving the polymer template.

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