

Studies on template-synthesized polypyrrole nanostructures

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Abstract The paper presents a short review of recent achievements in the rapidly growing field of the template synthesis of nanostructures together with their possible application. The results of our own work, concerning the polypyrrole nanotubules synthesis inside pores of track-etched membranes, have been presented as well. Finally, the kinetics of nanotubule growth process using the SEM method and permeability for air of the resulting structures has been also determined.

Key words template synthesis • track-etched membranes • polypyrrole nanotubules

Introduction

The template synthesis method based on deposition of materials inside well-defined uniform pores of isoporous membranes offers unique possibilities of manufacturing one-dimensional, high aspect ratio cylindrical species with lateral dimension below 100 nm, practically from any solid material. Rapidly growing interest in template-based synthesis is the result of search for novel methods of manufacturing materials with predefined shapes and dimensions in nanorange, preferentially based on assembling them directly from molecules. Such elements can be used further in the process of assembling final functional units. Such approach (called “bottom-up”) is completely different from the traditional method (called “up-down”) which is based on lithography, vapour deposition or chemical etching performed on materials of macroscopic scale. Such possibilities sketched for the first time by Feynmann in his talk to APS Meeting in 1959 [4] are now only partially explored, but it is expected that they will find broad applications in many areas of technologies (biotechnology, catalysis, optoelectronics, microelectronics, microcomputers etc.) in the nearest future. Traditional approach has been very effective since many years, e.g. in the case of integral schemes manufacturing (doubling of the number of gates on the chip every two years – so-called Moore’s law) but further continuation of this trend in the feature can be problematic due to the physical and

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technical limitations, e.g. high costs of deep ultraviolet or X-ray lithography.

Two types of available commercially templates are commonly used for nanomaterials synthesis – track-etched polymeric membranes (TMs) and anodic alumina oxide (AAO) membranes. TMs are obtained by irradiation of 10 μm thick polymer film (PET, PC) with cyclotron heavy ion beam and by chemical etching of latent tracks created during irradiation. Big areas of membranes are commercially available (width up to 600 mm with the porosity of about 12%). The main disadvantage of this kind of membrane is stochastic distribution of pores over the film area. The pore diameters depend on chemical etching conditions; the smallest available diameters are usually of about 50 nm.

The AAO membranes are obtained by anodic oxidation of aluminium foil in appropriate solution. During this process, highly ordered, closely packed array of columnar cells of pores with the walls made of aluminium oxide is created on the aluminium surface. The porosity of these membranes is much higher than in the case of TMs, amounting to about 66%. The pores are straight, perpendicular to the surface and having nearly hexagonal form. The diameter of pores depends on the conditions of electrochemical oxidation (applied voltage, kind of electrolyte solution) and can be varied in the range 100–500 nm. As was shown by Masuda [14], it is possible to obtain highly ordered network of pores on large areas by creating the regular texture on the aluminium surface by lithography or moulding process. Recently, it was shown [10] that creation of highly regular alumina structure is possible on the surface of silicon wafer patterned by lithography, chemically etched and covered with an aluminium layer of thickness about 400 nm by evaporation. The alumina structure matches exactly surface structure etched on the silicon wafer and has been used for synthesis of highly regular array of carbon nanotubes.

The template synthesis method has been developed rapidly during the last years and successfully applied to the synthesis of various one-dimensional nanostructures with lateral dimensions below 100 nm, having form of rods, wires, tubules, multiwall tubules and multilayer rods made of metals, semiconducting materials, carbon, metal oxides and polymers. The growing interest in this method has resulted in a large number of papers published during the last years. The review paper [6] summarises the results obtained before 2000. The recently published review paper [12] deals mostly with the synthesis of nanomaterials important for the modern electronics (carbon nanotubes, metallic nanowires, semiconducting materials, multi-layer GMR and spin-valve structures for spintronics). A review of novel electronic and optical properties of semiconducting nanowires and nanotubes resulting from their one-dimensionality and possible quantum confinement effects in two other dimensions has been reported in Ref. [16].

The template-synthesized nanotubes can find potential biomedical and biotechnological applications, e.g. as vehicles for delivery of drugs, DNA, proteins or other biomolecules. It has been shown [5] that using laboratory prepared AAO membranes and the sol-gel

method of silica deposition into pores of these membranes it was possible to synthesize silica tubular nanocapsules, open only at one end with controlled pore diameter (70 nm and 170 nm) and lengths (0.6 μm and 1.0 μm). Using well developed silane chemistry and commercially available reagents, it was possible to attach different chemical functional groups to outer and inner surfaces of silica nanotubes and making them lipophilic or lipophobic according to demands [7]. It is potentially possible to fill nanocapsules with the required drugs and tag their outer surface with antibodies that promote uptake by endothelial cells. Such system can be used for controlled drug delivery after successful solving the problem of capping and uncapping of open mouth of nanocapsules.

Another interesting field of applications is connected with separation of molecules and proteins on the basis of their sizes. It was shown [17] that by electroless deposition of gold to the pores walls of track-etched polycarbonate membrane, Au nanotubes membranes with the diameter of pores below 1 nm can be synthesised. At such small diameters, Au modified membranes show size-based selectivity in transport of molecules through the pores depending on ratio of molecule to pore diameter. Moreover, Au nanotubes membranes show ionic charge-based transport selectivity and can be switched between anion transporting and cation transporting state [15]. Furthermore, functionalization of inner surface of Au tubules by chemisorption of thiol-terminated poly(ethylene glycol) enables suppression of protein adsorption to the walls what makes them very attractive for separation purposes [11].

Different methods of deposition inside the pores are utilised, e.g. electrochemical deposition, electroless deposition, layer-by-layer self-assembly [9], surface sol-gel (SSG) deposition [8]. The last two techniques enable deposition of very thin films. This opens very interesting perspective of obtaining a catalytic membrane having the pore walls covered by thin layer or islands of catalytic material. The template deposition for obtaining novel types membranes suitable for application in catalysis and in fine size-based filtration of macromolecules as well as using of ionising radiation for nanostructures creation and modification is our long-term research goal [2, 3].

The kinetics of deposition process into pores of nanoporous membrane is still not well-understood. In many experiments on deposition into the pores, an observation has been made that chemical properties of pore walls (chemical groups present on the surface) play an important role in kinetics of the deposition process, in particular, during its initial step. In the present paper the kinetics of deposition of conducting polymer inside TMs is described.

Experimental and results

Polypyrrole (PPy) belongs to conducting polymers which are the most stable in typical environmental conditions. PPy can be prepared by electrochemical or chemical oxidative polymerization where ferric chloride is the initiator of choice that also acts as the dopant. In

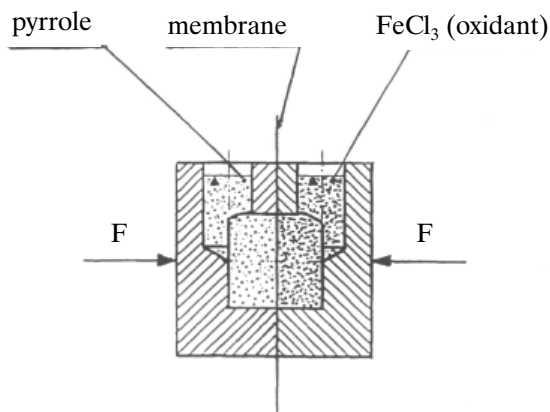


Fig. 1. A scheme of the set-up for formation of PPy nanotubes inside of TMs pores.

the present work, the template-based synthesis of PPy was carried out inside pores of track-etched membranes made of a 10 μm thick poly(ethylene terephthalate) (PET) film (received from the Joint Institute for Nuclear Research, Dubna, Russia). Due to such features as: precise determined pores diameter, smooth surface, high chemical and thermal resistance, TMs are good material as templates [1].

Such polymers as mentioned above should have predictable area and controlled morphology. This required some investigations concerning the mechanism of formation PPy surface and kinetics of polymerization process inside pores of a template.

In experiments, two kinds of TMs described above with pores diameter: 0.2 and 1.3 μm have been applied for PPy synthesis, aqueous solutions: 0.1 M pyrrole and 0.3 M FeCl_3 (III) as oxidants have been used [13, 18]. In the course of experiments, the above solutions were introduced to both sides of a membrane disc, that had been mounted in a plexiglas mould (Fig. 1). The diameter of the disc was equal to 25 mm.

In the process of synthesis, PPy was deposited inside the pores and on the membrane surfaces. Time of this process has been changed from 7 up to 45 min. Thickness of PPy nanotubes inside the pores and PPy layers on surfaces were determined by using a scanning electron microscope (SEM) Zeiss-Leo DS 942 type. Selected SEM photographs (Figs. 2 and 3) show the nanotubes formed in two kinds of templates (TMs with pores 0.2 and 1.3 μm) after different times of process: 15, 21 min and 15, 30 min, respectively. It can be observed that nanotubes give mapping of inside pore structure. Figure 4 shows the SEM photographs of PPy layer on the membrane surface from pyrrole solution side (a) and from ferric chloride solution side (b). Such photographs permitted to determine thickness of the above layers.

SEM measurements allowed also to determine nanotubule wall thickness vs. time of PPy deposition inside pores in case of two kinds of TMs (Fig. 5). One can see that for membranes with pore size 0.2 μm in case of time period 7–45 min there is a linear dependence of thickness growth as well as for membrane – 1.3 μm in case of time period 7–30 min. Analysing graphs in Fig. 5, two stages of PPy nanotubules growth can be described: the faster first stage during the first 7 min and the next slower one. For the second stage, values of growth speed are equal to 1.4 nm/min and 4.9 nm/min, respectively (for both kinds of templates).

The permeability for the above samples was determined at an air pressure of 0.5 bar. For TMs with pore size 0.2 μm , the permeability was equal to 0.70 l/(min·cm²). Values of permeability for different PPy nanotubules deposited in such pores are given in Table 1. It was calculated that by decreasing the internal pore diameter by 6.3 times (from 200 to 32 nm), the permeability decreased by 2.9 times.

For TMs with pores size 1.3 μm , the permeability was equal to 14.8 l/(min·cm²). For different PPy nanotubules deposited in pores, the permeability is given in

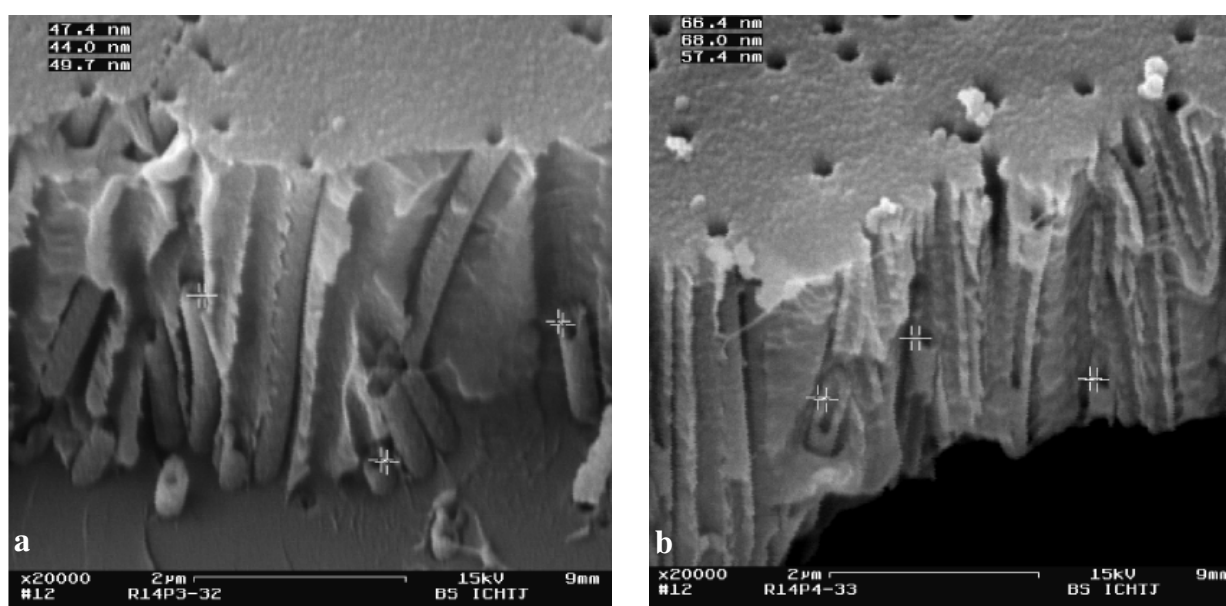


Fig. 2. Nanotubules formed in pore of TM membrane (0.2 μm pore size) after 15 min (a) and 21 min (b) of polymerization process.

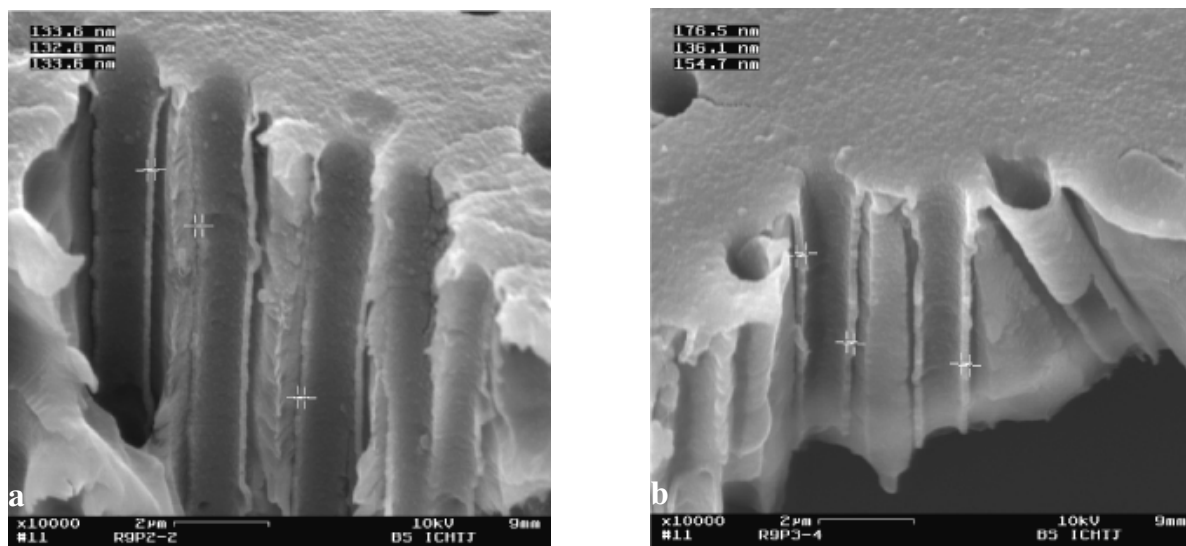


Fig. 3. Nanotubes formed in pores of TM membrane (1.3 μm pore size) obtained after 15 min (a) and 30 min (b) of polymerization process.

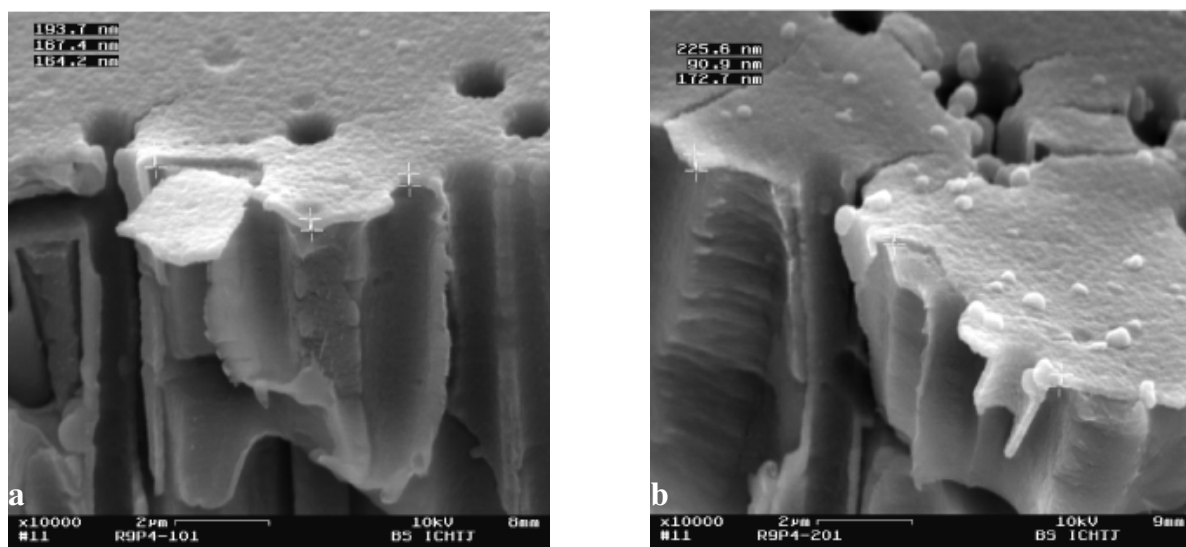


Fig. 4. PPy layers on the surfaces of TM membrane (1.3 μm pores size) after 30 min of polymerization process: (a) on the side in contact with the pyrrole solution; (b) on the side in contact with the FeCl_3 solution.

Table 2. In this case, decreasing the internal pore diameter by 6.6 times (from 1300 to 198 nm) causes the permeability to decrease by 10.4 times.

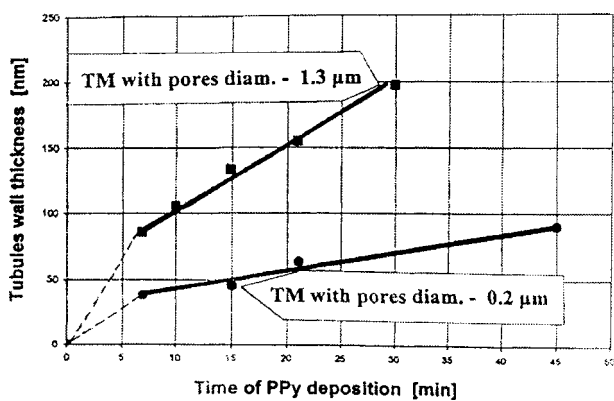


Fig. 5. Kinetics curves of PPy nanotubes growth inside the pores.

Table 1. Permeability of nanotubes deposited in pores of TMs 0.2 μm at air pressure of 0.5 bar

| Wall thickness of nanotubes [nm] | Internal diameter of nanotubes [nm] | Permeability [$\text{l}/(\text{min}\cdot\text{cm}^2)$] |
|----------------------------------|-------------------------------------|--|
| 25 | 110 | 0.56 |
| 40 | 80 | 0.33 |
| 64 | 32 | 0.25 |

Table 2. Permeability of nanotubes deposited in pores of TMs 1.3 μm at air pressure of 0.5 bar

| Wall thickness of nanotubes [nm] | Internal diameter of nanotubes [nm] | Permeability [$\text{l}/(\text{min}\cdot\text{cm}^2)$] |
|----------------------------------|-------------------------------------|--|
| 107.6 | 1085 | 7.36 |
| 155.7 | 989 | 4.50 |
| 197.7 | 905 | 1.42 |

Conclusions

- Track-etched membranes with pores diameter in the range 0.2–1.3 μm have been successfully used as templates for preparation of polypyrrole nanotubes.
- Kinetics of nanotubules growth in membranes pores has been determined. Two stages of nanotubules wall thickness growing vs. time were observed; first – fast lasting up to 7 min from the beginning and then – slower, approximately linear. Knowledge of this gives the possibility to synthesize polypyrrole nanotubules with predetermined geometry.
- Permeability of modified track-etched membranes containing PPy nanotubules has been determined what seems to be an important parameter for applications.

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