RADIATION USE IN PRODUCING TRACK-ETCHED MEMBRANES

Wojciech Starosta

Institute of Nuclear Chemistry and Technology, Dorodna 16, 03-195 Warszawa, Poland

1. INTRODUCTION

Track-etched membranes are thin polymer films which have a system of fine, geometrically well-defined pores. A two-step process is used to achieve this. The first step consists of a thin polymer film being irradiated with a high energy heavy ion beam. During this step heavy ions penetrate the polymer film depositing part of their energy that results in ionization and excitation of target electrons. Because of the high energy depositions per unit length, discrete cylindrical regions extending along the ion trajectories and containing highly excited matter are formed. Through sequential relaxation steps, primary excitation energy is redistributed to electrons and ions in the film through a series of elemental processes involving the creation of radicals, of chemical bond breaking, of chain scissioning, the creation of small size chemical species, of gaseous product evolution (e.g. hydrogen) and of crosslinked fragments that finally lead to severe degradation of polymer chains inside the excited regions, which are called latent tracks [1-3]. In the second step, damaged polymer chains remaining after ion passage are etched using suitable chemicals to remove small size particles outside of the track by diffusion [4]. Assuming symmetrical etching conditions (etching from both sides of the film), cylindrical pores are formed, with the diameter dependent on the etching time.

Figure 1 is a scheme showing the pristine semicrystalline polymer (Fig.1A) and tracks created after the heavy ion passage through the polymer (Fig.1B). The reduced core density containing broken polymer chains and a hallo zone consisting of crosslinked polymer strands are illustrated (Fig.1B).

In Fig.2 the general photomicrographs of a final track-etched membrane made of poly(ethylene terephthalate) (PET) film are shown: the general view of the film surface (Fig.2A) and the cross-section view (Fig.2B).



Fig.1. Scheme of ion tracks in a polymer: (A) initial semicrystalline polymer; (B) track consisting of a reduced core density, containing broken polymer strands surrounded by a track hallo zone crosslinked polymer strands. (Reproduced from Ref. [1]).

The phenomenon of track development in dielectrics were first documented in Young's paper published in *Nature* in 1958 [5]. Young noted that the heavy ions created as the result of uranium fission by slow neutrons, having a broad spectrum of energies, could be used for LiF irradiation. Track etching had been shown after contact with a strong alkali and tracks could be seen with an optical microscope. Further studies in this field were carried out by Price and Walker using mica irradiated with heavy ions from uranium fission. They patented their discovery entitled "The molecular sieves and the method of producing the same" in 1962 [6]. Shortly thereafter, the possibility of precise track etching in plastic materials was described in a paper by Fleischer and Price published in *Science* in 1963 [7]. The early researchers in track etching noted a broad scope of potential applications for etched tracks. Potential applications considered at that time included the determination of the age of geological and archaeological specimens containing natural uranium, the study of the early history of the solar system as recorded in meteorites, the determi-



Fig.2. SEM (scanning electron microscopy) photomicrographs of a surface (A) and of a cross-section of track-etched membrane (B) made from a PET film.

nation of charged particle fluxes, the separation of biological cells having different sizes, aerosol sampling, *etc*.

The discovery of track etching to create pores in irradiated polymers was soon commercialized by the Nuclepore Company. Nuclepore track-etched polycarbonate membranes were manufactured from thin polycarbonate film irradiated with neutron-induced uranium fission products.

The major step in the advancement of track-etched technology was achieved around 1970 because of the developments in heavy ion accelerator technology. Heavy ion monoenergetic beams of multiple-charged ions, with precisely determined energy and mass, operated in a scanned mode, could be used for polymer film irradiation. The use of accelerator ion beams instead of uranium fission fragments enabled the irradiation of thicker polymer films and manufacture of pores of precise uniform diameter with controlled porosity and orientation – perpendicular or intentionally inclined to the surface of the film. Accelerator produced membranes were free of any possible radioactive contamination from fission fragments.

From then on, particle track-etched membranes have been routinely produced using heavy ion beam accelerators. Since 1970, polyester track-etched micro- and nanoporous membranes have been manufactured by the Flerov Laboratory of Nuclear Reactions, Joint Institute for Nuclear Research (JINR) in Dubna, Russia, using a heavy ion cyclotron. Other companies, as it4ip (a spin off from the Université Catholique de Louvain, Belgium), offer membranes made of polyester (PET), polycarbonate (PC) and polyimide (PI) films. Cyclopore and Poretics are other trademarks for these membranes. Research has been conducted in this field for many years by GSI Darmstadt, Germany.

Track-etched membranes possess a number of unique structural features that have made them distinct in comparison to other polymeric membranes, for example well-defined cylindrical geometry of pores, precise pore diameters and narrow pore size distributions enabling the exact exclusion limit in the case of particle filtration. At present, track-etched membranes made of polyester, polycarbonate or polyimide films are commercially available from the number of companies in a range of pore sizes, porosities and thicknesses. The key features of track-etched membranes are the following:

- well-defined cylindrical geometry of pores in the range of 10 nm to few μm,
- standard thicknesses in the range of 10-25 μm,
- narrow pore size distribution (variance of pore sizes below 5%),
- porosity in the range of 1-20%,
- low protein binding and low extractability ensuring no sample contamination,
- smooth and flat surfaces enabling particle collection for microscopic observation,

 chemical inertness and good thermal stability (up to 430°C in the case of membranes made from polyimide film).

Etched heavy ion tracks in polymers are suitable for a number of interdisciplinary uses in diverse fields. Track-etched membranes perform very well in applications where their unique structural properties are fully used. Due to their exact cut-off size, they perform well in the fine cleaning of small volumes of high value fluids from particulate material. They can be used for the efficient separation of medical and biological liquids from bacteria when a membrane with appropriate pore diameter is selected. In biosensors, they can be used for the controlled diffusion of biochemical reagents and for the protection of electrochemical detectors [8]. Due to their smooth surfaces, they can be used in the cell culture technologies for membrane-supported cell culture [9], cell nutrition, and cell collection by filtration for microscopic observation. The smooth surfaces are suitable for sample preparation for SEM (bacterial or air particulate matter analysis) and related analytical techniques.

A new area of use related to template synthesis of materials has emerged. In template synthesis, the cylindrical pores of track-etched membranes are used to directly deposit various materials inside the pores, such as polymers, metals or metal oxides. Monodispersed, one-dimensional nanostructures in the form of nanorods or nanotubes with a high length to diameter ratio and a strictly controlled radius by the membrane pore diameter can be made by this method [10-14]. Different architectures of nanostructures are possible. Materials may be left in the membrane which results in a flexible material with the filled pores. After the membrane polymer is dissolved, the discrete nanoparticles can be recovered by filtration for further use. When the membrane fixed to the solid support is filled and then dissolved after being made, brush-like nanostructures can be formed. Interest in one-dimensional structures stems from the fact that their physicochemical properties usually greatly differ in comparison to the properties of bulk structures and they can be used in the manufacture of electronics and sensors [15]. Such high aspect ratio nanostructures with length to diameter ratios reaching 1000 were not possible using standard methods of nanolithography based on ultraviolet (UV) or X-ray exposure.

There is a growing interest in track-etched pores in different areas of biology and medicine, where small diameter nanopores can be used as artificial model channels mimicking these encountered in biological membranes [16, 17]. Due to the higher stability of artificial channels, they can be used for the study of diverse biological processes, *e.g.* selective ion transport through the pores. Another broad area of use in biology is cell culture. There is also a growing interest in the development of microfluidic chips where membranes support cell cultures to simulate *in vivo* conditions. The microfluidic module presented in Ref. [9] consists of a fluidic supply channel and a cell culture chamber separated by a thin, low-dead-volume porous membrane (pore size -0.015-0.2 µm). On one hand, these membranes serve as a physical barrier for a sus-

pended cell culture against contaminants. On the other hand, the membrane permits controlled exposure of the cells to various concentrations of a drug that is transported *via* nanochannels through the membrane to interact with the cells. Such platforms should allow monitoring of various physiological processes and provide a large degree of freedom in the control of experimental conditions, while using reduced volumes of reagents and cells. These devices show great promise for high-throughput, automated drug screening in a point-of-care environment by relatively unskilled users.

It has been shown that diverse forms of the pores can be made, *e.g.* conical, cigar-like or a bowl-like shape, by properly choosing the etching process (asymmetrical, one-side etching or by adding surfactants on the one side of etched membrane) [18]. Detailed studies have confirmed the presence of charged species on the pore surfaces, resulting from polymer bonds being broken resulting in the formation of carboxylic or hydroxyl groups. This is important since pores with small diameters having charged groups on the pore surface can significantly influence the ion transport through the nanochannels, enhancing transport of counter-ions and diminishing transport of co-ions. The mechanism of ion and molecular transport through narrow channels is of great importance for biological studies. The developments achieved in track-etched techniques enable the making of artificial nanochannels, which better mimic those in the real biological world [19-24].

Another promising area of use for the track-etching technique is lithography. In the case of lithography based on ion beams, it is possible to create sub-100 nm features down to 10 nm in silicon and in polymers, which are not attainable using traditional optical lithography due to diffraction effects [25]. Different techniques can be used for making nanostructures, such as: ion projection lithography (IPL) and focused ion beam (FIB). The IPL technique follows traditional lithography, using large area masks through which a pattern is replicated in a resist material. In IPL, the complete absence of diffraction effects, the ability to tailor the depth of ion penetration to suit the resist thickness or the depth of modification, and the ability to pattern a large area in a single brief irradiation exposure without any wet processing are the prime characteristics of this technique. Ion tracks, specifically etched tracks, alone or in combination with lithography, enable many possibilities for creating novel deep micro- and nanostructures within polymer films that are difficult to produce or even unattainable by other techniques. Prototypes of a number of ion track-based electronic components, such as resistors, diodes, capacitors, magnets, transformers, transistors, and several types of sensors, have been made. The first hybrid track-based silicon polymer device has been successfully tested. However, this is still a long way to the industrial use. Nevertheless, the potential use of ion track-based microporous films is tremendous [26].

2. TRACK-ETCHED MEMBRANE MANUFACTURING

The manufacture of track membrane is the two-step process. In the first stage, polymer films are irradiated with heavy ions. The two typical methods of irradiation are shown in Fig.3. Figure 3A shows the irradiation with uranium fission products which were used at the early stages of research into track-etched materials, and Fig.3B shows the irradiation with an ion accelerator beam in the scan mode, as presently used. A special mode of beam scanning permits single



Fig.3. Scheme of irradiation of polymer films with uranium fission fragments (A) and heavy ion accelerator beam in scanning mode (B). (Reproduced from Ref. [2]).

ion track irradiation [27]. In that case, a low intensity beam is used and the irradiation is stopped immediately after the first ion pass through the film is detected. This variant of irradiation is used mainly for single track membrane preparation which is needed for high level research on ion transport phenomena inside a single pore and for different biological sensors manufacture. Recently, the preparation of single or few ion tracks based on a scanning ion beam has been achieved using set of small diameter diaphragms placed in the front of the film [28].

While passing through a polymer film, heavy ions interact with the target nuclei and with target electrons. Such interactions can be described as series of discrete binary collision events, each one governed by electrostatic force of interaction between the charged particles, as described by Coulomb law. According to the rules of classical mechanic (conservation of energy and momentum), part of the energy of primary particle is transferred to the target particle and the incident particle is deflected from its primary direction. However, the details of these processes depend strongly on the specific energy (energy per unit mass) of the primary particle and on the mass ratio between the colliding particles. The transfer of energy to the target nuclei prevails at low values for ion specific energy (0.001 MeV/nucleon) and the transfer to target electrons prevails at higher specific energy values (at around few MeV/nucleon). This is shown for the case of Xe ions in PET films (Mylar) in Fig.4.



Specific energy MeV/nucleon

Fig.4. Dependence of energy losses per unit length for Xe ions with different specific energies penetrating PET film (Mylar). The functions were calculated using SRIM2013 software [29].

For the track-etched membrane manufacturing, heavy ions with sufficiently high specific energy are used, around 2 MeV/nucleon and higher. In this case, the transfer of energy in collisions with the nuclei can be neglected. Due to the large difference in the masses of electrons and ions, heavy ions do not change their direction in successive collisions and move approximately along a straight line. The quantitative description of the stopping of a heavy ion in matter is the energy loss per unit length. The electronic energy losses to target electrons per unit length are described by Bethe-Bloch formula:

$$-\frac{\mathrm{dE}}{\mathrm{dx}} = \frac{4\pi \mathrm{N}_{\mathrm{A}} Z\rho}{\mathrm{Am}_{\mathrm{m}} \mathrm{m}_{\mathrm{e}} \mathrm{c}^{2}} \left(\frac{\mathrm{e}^{2}}{4\pi\varepsilon_{0}}\right)^{2} \frac{\mathrm{z}^{2}}{\beta^{2}} \left[\frac{1}{2} \ln\left(\frac{2\mathrm{m}_{\mathrm{e}} \mathrm{c}^{2}\beta^{2} \mathrm{T}_{\mathrm{max}}}{(1-\beta^{2}) \mathrm{I}^{2}}\right)\right] - \beta^{2} - \frac{\delta}{2}$$

where: Z – charge of ion, β – velocity of ion in light velocity unit (v/c), I – target ionization potential, T_{max} – maximum energy transfer to target, m_e – electron mass, M – ion mass, γ – relativistic factor. T_{max} is available from the following equation:

$$T_{max} = \frac{2m_e c^2 \beta^2 \gamma^2}{1 + 2\gamma m_e / M + (m_e / M)^2}$$

where $\gamma = 1/\sqrt{(1-\beta^2)}$.

The energy deposited per unit length is related directly to the density of damaged polymer chains along the ion trajectory. The dependence between the density of energy deposition and the density of defects is a complex nonlinear relation. The process of ion interaction with a stopping material is statistical in nature, so there should be fluctuations in linear energy deposition. Correspondingly, fluctuations in the length of primary damaged micro-regions along the ion trajectory are expected. At sufficiently high values for the energy deposited



Fig.5. (A) Energy loss as a function of specific ion energy. The dashed lines separate the different regimes of track etching: homogeneous (full symbols), inhomogeneous (crossed symbols), and absence of etching (open symbols). (B) SEM images of uniform pores resulting from homogeneous tracks (left) and pores with broad size distribution due to inhomogeneous tracks (right). (Reproduced from Ref. [30]).

per unit length, the fluctuations will be smoothed and the overlapping of damaged micrograins can occur giving a continuous cylindrically shaped damaged latent track prior to the etching. It was experimentally found and reported in the literature that for the creation of continuous etchable latent ion tracks in polymer films able to perform as membranes, the energy deposition per unit length should be higher than some threshold estimated at 720-900 eV/nm for polycarbonate, polyimide and poly(ethylene terephthalate) [30].

To get an idea of possible quantitative energy depositions, the energy loss for four ions – Xe, Kr, Ar and O, were calculated using the SRIM software [29] and are presented in Fig.5. The dashed horizontal lines drawn at different values for energy losses separate the different regimes of track etching: homogeneous, inhomogeneous, and no etching.

The energy loss curves reach a maximum in the range of 1-5 MeV/u, depending on the ion type. Accelerated ions with specific energy in this range are the most efficient in energy deposition to a polymer target considering the deposited energy value and uniformity of linear energy deposition along the ion trajectory. For the case of the Xe ion with a specific energy of 3 MeV/u, linear energy deposition reaches the value of 1200 eV/Å and the range of the nearly uniform linear energy loss is sufficiently long, reaching about 20 μ m as shown in Fig.6. Considering that the typical energy required to chain scission in polymers is in the range of 100 eV, severe damage to a polymer would be expected.



Fig.6. The energy loss of a light (atomic number Z = 36, atomic mass A = 92, energy E = 101 MeV) and a heavy (Z = 56, A = 141, E = 65 MeV) fission fragment of ²³⁵U as a function of the range in poly(ethylene terephthalate). A curve for an accelerated Xe ion (Z = 54, A = 132, E = 396 MeV) is also shown. These curves were calculated using the stopping and ranges of ions in matter using the SRIM2013 code [29].

The structure of the damaged region is complex. However, the energetic electrons created in the primary processes of interaction (called δ -electrons), emitted mainly in the directions perpendicular to ion trajectory, can interact with matter further, leading to the creation of the electron cascades in the region surrounding the primary region of interactions. This process is connected with further ionization and excitation of atoms inside this region by direct electron impact or accompanying Auger relaxation processes of excited ions. As the result of these processes, the radii of severely damaged regions are extended up to 20 nm and a so-called halo region is formed around the track core. Therefore, the primary processes are completed with the central regions highly excited and electron clouds somehow shifted outside these regions. Next, the excitation energy is equilibrated in the relaxation processes in short time-scale of a femtosecond. The details of the relaxation of this far from equilibrium state are still under discussion. The difficulties in finding adequate theory are related to the proper description of the relaxation kinetics for the far from equilibrium state resulting from a high density of energy deposited into very small volume. The relaxation of these far from equilibrium states proceeds through cooperative action involving target electrons and ions leading to severe structural changes inside the primary damaged region and in the close vicinity around them, as a result of degradation of polymer chains through radical creation, chain scissioning, and chain crosslinking. Commonly used models for relaxation were elaborated on in early studies of track formation and include Coulomb explosion and a thermal spike model [1]. The first one takes into account the strong repulsive forces acting between ions remaining inside the track core while energetic electrons where moved outside. This interaction leads to rapid, explosive expansion of ions by atomic collision which cascades in the vicinity of the ion trajectory. The thermal spike model takes into account the rapid temperature rise inside the core at the ion passage step which leads to melting and disorder.

In the case of polymers the track core region undergoes severe structural transformation because of a chemical reaction initiated by radicals inside the core. Chain scission prevails inside the core, while outside the core in the track halo region (diameter – 10-100 nm) electron-induced radiation effects dominate, sometimes forming a crosslinked layer around the track core. Breaking of the most of the covalent bonds in the track core (including both the polymer backbone and side groups) is accompanied by around a 10% reduction of the density, which means that the free volume has increased proportionally. In polymers containing hydrogen, this local zone is depleted of hydrogen atoms, so unsaturated carbon–carbon bonds form. After the physical stage of track formation has been completed, the track in the polymer undergoes relatively slow chemical transformations, such as the decay of radiolysis intermediates, reactions with air (primarily oxygen), and creation of new groups (*e.g.* peroxide, hydroyen) that enhance preferential etching.

Chapter 18

Due to these structural changes accompanied by the formation of reduced density zones, the fast penetration of suitable chemical etchants are facilitated along the track enabling further degradation of oligomers present inside the track through chemical reactions initiated by etchant. Small weight clusters created in the etching process are removed to the outside by diffusion. The structural changes inside the track core enable the etching of the track. The free volume in the track core facilitates the penetration of the chemical reagent (etchant) along the particle's path and accelerates the chemical degradation of the macromolecular segments located there. In contrast, the modification of the polymer properties in the halo is not as strong. A typical feature of many polymers is that the halo material is etched at a lower rate than the pristine polymer. This phenomenon is likely caused by the preferential crosslinking of macromolecules in the halo region around the track core.

Chain scissioning in the latent tracks results in monomer segments at the end of a chain and only one chemical cleavage is required for etching. This simpler process contributes to the higher etch rate in the track. In addition, the etchant can diffuse faster into the track than into the non-tracked material. A combination of these effects qualitatively explains the much higher etch rates for the tracks compared to non-tracked materials.

The next stage of track-etched membrane manufacturing process consists of track sensitization using UV irradiation of the films. The stability of latent track and their susceptibility to etching can be increased by exposure to UV radiation in air. With a suitable chosen UV wavelength, a remarkable increase in etching rate along the track can be achieved with a minor effect on etching rate of the bulk polymer matrix. The mechanism responsible for that effect is



Fig.7. General scheme for track-etched membranes manufacturing. (Reproduced from Ref. [2]).

related to the photodecomposition of radiolysis products formed during heavy ion passage into low molecular weight species [31].

The final stage in track-etched membrane manufacturing is related to the etching of latent tracks with the irradiated film passing through the bath containing the etch solution. A typical scheme for this etching procedure is shown in Fig.7.

The process of etching consists of the penetration of a small-sized etchant molecules into the track core and in the selective breaking of chemical bonds inside the degraded core by chemical reactions [4]. Small size atomic clusters created in this process can be removed to the outside of the track by diffusion. The etching process is based essentially on two factors. One is related to large differences in the velocities for etching along the track core and in direction perpendicular to the track axis due to the easier transport of small etchant molecules in the less compact structure of the core. The second factor is kinetic in nature and is related to the lower chemical barriers for chemical bonds to break by reaction of the etchant with small low molecular weight units present in partially degraded core. Two values describe the kinetics of etching process: velocity of etching along the track, v_t , and velocity of etching for the unirradiated bulk matrix, v_b . For PET, the alkali etching solution is applied at temperatures in the range 50-80°C. The ratio of track to bulk etch velocities can reach up to 1000.

In PET etching, the mechanism is based on the alkaline cleavage of ester bonds. The corresponding chemical reaction scheme is shown in Fig.8. The free ethylene glycol and anion of terephthalic acid molecules as well as the bonded end groups, both carboxylate and hydroxyl, are created as the reaction products. It is worth noting that the pendant ionizable bonds present on the pore walls make them electrically active and are responsible for the selective ion transport through the small radius pore in an electrolytic solutions. This unique property in combination with the small pore radius is used for the selective sensing of macromolecule passage through the pore on the basis of current blockage in electrolyte solution.



Fig.8. Chemical reaction scheme for ester bond cleavage in PET.

In large-scale track-etched membrane manufacturing, symmetrical etching conditions are used. In this case, the liquid etchant equally accesses both sides of the polymer film that is submerged in the etching bath. Due to the high



Fig.9. Scheme of track etching of irradiated film in the presence of nano-sized surfactant molecules. (Reproduced from Ref. [33]).



Fig.10. SEM micrographs of membranes with a conical pore (A), a bullet-like shape (B) and an hour glass (C) form.

427

value of the etch ratio, cylindrically shaped pores are created with diameters depending on the time of etching. On a laboratory scale, asymmetric etching conditions can be applied in order to get non-cylindrically shaped pores. In this case, one side of the membrane is in contact with etchant solution while other side is in contact with a so-called stopping solution containing an acid neutralizing solution. By this method, conical pores with small openings can be manufactured, which have found use as model systems for selective ion transport studies in electrolytic solutions and for single macromolecule detection.

Another possibility for the modification of the track form is the application of a surfactant solution on one side of membrane, as shown in Fig.9 [27, 32]. The surfactant diffusing through the openings made in the etching process binds to the surface of tracks and block them from etch attack. The detailed form of pore depends on balance of the surface coverage by the surfactant and by the etchant. Pores with the various forms, such as narrow and wide cones, spherical troughs, barrels, and bottle necked structures, can be obtained by this method. Some of them are shown in Fig.10.

3. APPLICATIONS OF TRACK-ETCHED MEMBRANES

3.1. TEMPLATES FOR ONE-DIMENSIONAL MATERIALS

The unique properties of track-etched membranes having well-defined shapes and precise pore diameters make them very attractive as hard templates for making one-dimensional, high aspect ratio nanomaterials like nanowires and nanotubes. Materials can be made from polymers, metals or metal oxides with diameters in the range of 10-200 nm and lengths of 10 μ m. This gives a length to diameter ratio of up to 1000. In comparison to another well-known hard templates, like anodic alumina oxide membranes made by the electrolytic oxidation of aluminium foils, polymer track-etched membranes have a much wider range of pore diameters.

The template method is used to make free-standing arrays of one-dimensional materials in polymer films. After chemical dissolution of the polymer matrix, the nanoparticles can be recovered by filtration. A variation is the immobilization of arrays fixed on silicon/silicon oxide support covered with a conducting Au (or Pd) layer and spin coated with a thin polymer film for track etching.

Interest in exceedingly small dimensional materials is being driven by two stimuli. The first is related to the fact that physical and chemical properties become different at very small dimensions in comparison those of large bulk particles. The second is a common trend toward miniaturization in the field of

Chapter 18

sensing elements and a tendency to develop sensors operating at atomic scale level. In the case of sufficiently small diameter particles, a large fraction of atoms is lying on the surface occupying under-coordinated surface reactive sites. Attachment of external molecules on the surface of a semiconductor nanowire can strongly influence its conductivity due to the redistribution of the charge inside the nanowire needed to screen external molecular charges [34]. This happens when the Debye length for nanowire, the parameter describing the extension of electric field penetration into the bulk, is comparable to the diameter of nanowire. In the case of photosensitive materials, a relaxation processes of charge carriers generated by photon absorption depend strongly on the dimension of the absorbing particle. The time needed for photoinduced carriers to reach the surface by diffusion can be shorter than the hole-electron recombination time. Thus, a redox reaction on the surface would be possible with the participation of photogenerated charge carriers. Such a property is important for the photooxidation processes or, in the case of conductometric sensors, for their recovery and time response in the case of photoinduced analyte desorption. Thus, metal-oxide nanowires can function as sensitive and selective chemical or biological sensors. The active nanowire sensors in such devices can be configured either as resistors, whose conductance is altered by charge-transfer processes occurring at their surfaces or as field-effect transistors whose properties can be controlled by applying an appropriate potential onto a gate. Functionalizing the surface of these entities offers yet another way for expanding their sensing capability. Although research on the use of metal--oxide nanowires as sensors is still in its early stages, several encouraging experiments have been reported that are interesting in their own right and indicative of a promising future [35-38].

The template synthesis method of nanomaterials using track-etched membranes was pioneered by the Charles Martin's group at the University of Florida [39]. Their research has been directed to application of template made nanotubes and nanotube membranes for biosensors and for macromolecule detection and separation [8, 10, 13, 22]. At present, the template method for track-etched polymer membranes has become a mature method and is widely used by many research groups.

Various methods are used for making templates: electrochemical deposition in the case of metals, electrophoretic deposition in the case of non-conducting materials, vapour deposition, electroless deposition and chemical deposition from solution.

Table 1 presents information on materials and methods used for making nanostructures taken from recently published papers.

Electrochemical deposition proceeds according to the scheme shown in Fig.11. One face of the template must be covered with an inert conducting film (*e.g.* gold or platinum) serving as the anode. The metal is then electrochemically deposited within the pores of the membrane. The length of the nanowires

Table 1. Examples of nanostructures made by the membrane template methods.

No.	Product type	Membrane material	Technique	Ref.
1	Ni nanowires on Si/SiO ₂ substrate, diameter $-20-60$ nm, length $-2 \ \mu m$	Polycarbonate	Electrodeposition	[40]
2	Bi single wire, cylindrical, conical	Polycarbonate	Electrodeposition	[41]
3	Ni, Co, Cu, Au, polypyrrole nanowires	Polycarbonate	Electrodeposition	[42]
4	Co, Ni-Au bisegment nanowires; NiFe/Cu/NiFe, Co/Cu/Co trisegment nanowires	Polycarbonate	Electrodeposition	[43]
5	Cu single nanowires, length – $30 \ \mu m$	Polycarbonate	Electrodeposition	[44]
6	Cu nanowires, diameter $-$ 0.2 and 0.4 $\mu m,$ length $-$ 10 μm	Polycarbonate	Electrodeposition	[45]
7	Au, poly- and single crystalline nanowires, length – 25 μm	Polycarbonate	Electrodeposition	[46]
8	FeNi (permalloy Ni ₈₀ Fe ₂₀), Cu, Au nanowires	Polycarbonate	Electrodeposition	[47]
9	Au, conical nanowires	Polycarbonate	Electrodeposition	[48]
10	Au, Ag, Cu, Ni, Co, Rh, diameter – 40 nm, length – 3-5 μm	Polycarbonate	Electrodeposition	[49]
11	Au, Cu, Pt, Bi, Bi ₂ O ₃ , ZnO, CdTe nanowires	Polycarbonate	Electrodeposition	[50]
12	Bi ₂ Te ₃	Polycarbonate	Electrodeposition	[51]
13	Ni-CdTe, Ni-ZnO-Ni multisegment nanowires	Polycarbonate	Electrodeposition	[52]
14	$Pb(Zr_{x}Ti_{1-x})O_{3}$ nanowires, diameter – 100 and 200 nm	Polycarbonate	Electrophoretic deposition	[53]
15	$\begin{array}{l} TiO_2, SiO_2, BaTiO_3, Sr_2Nb_2O_7, Pb(Zr_{0.52}Ti_{0.48})O_3,\\ diameter-45\text{-}200 \text{ nm}, length-10 \ \mu\text{m} \end{array}$	Polycarbonate	Electrophoretic deposition	[54]
16	TiO_2 , diameter – 45-200 nm, length – 10 μ m	Polycarbonate	Electrophoretic deposition	[55]
17	TiO_2 , diameter – 200 nm	Polycarbonate	Electrophoretic deposition	[56]
18	SiO_2 nanotubes, diameter – 100 nm	Polycarbonate	Atomic layer deposition	[57]
19	Al ₂ O ₃ layer on conical nanochannels	PET	Atomic layer deposition	[58]
20	TiO_2 film, diameter – 200 and 400 nm, length – 10 μ m	Polycarbonate	Atomic layer deposition	[59]
21	Fluorinated polymer layer, diameter – 50 nm	Polycarbonate	Chemical vapour deposition	[60]
22	Al_2O_3 film	PET	Atomic layer deposition	[61]

Chapter 18

Table 1. Contd.

No.	Product type	Membrane material	Technique	Ref.
23	TiO ₂ , SiO ₂ , Al ₂ O ₃ films, diameter – 18-55 nm, thickness – 5-22 nm	Polycarbonate	Atomic layer deposition	[62]
24	Au	Polycarbonate	Electroless deposition	[63]
25	TiO_2 , length – up to 30 μ m	Polycarbonate	Electroless deposition	[64]
26	Pt nanotubes, Pt/Ru bimetallic nanotubes	Polycarbonate	Electroless deposition	[65]
27	Ni, Ni-B nanotubes	Polycarbonate PET up to 30 µm	Electroless deposition	[66]
28	Ag film; Pt, Cu nanotubes	Polycarbonate	Electroless deposition	[67]
29	Au nanowires for DNA immobilization, diameter – 10 nm	Polycarbonate	Electroless deposition	[68]
30	Pd nanotubes, length – $30 \ \mu m$	Polycarbonate	Electroless deposition	[69]
31	Au nanowires array	Polycarbonate	Electroless deposition	[70]
32	Ni, Pt, Cu, Ag, Au network, pore diameter – 400 nm	Polycarbonate	Electroless deposition	[71]
33	Au film functionalized with fluorinated thiols	Polycarbonate	Electroless deposition	[72]
34	Ag nanoparticles; Au, Cu, Pt nanotubes	Polycarbonate	Electroless deposition	[73]
35	Ni nanotubes, length – 10-100 μ m	Polycarbonate	Electroless deposition	[74]
36	Au nanotube membrane, diameter – 50 nm	Polycarbonate	Electroless deposition	[75]
37	Ag microtubes, length – $10 \ \mu m$	Polycarbonate	Electroless deposition	[76]
38	Cu doped Zn nanorods	Polycarbonate	Chemical solution	[77]
39	MgO nanorods, diameter – 70-160 nm, length – 5-6 μm	Polycarbonate	Chemical solution	[78]
40	In_2O_3 nanorods, diameter – 0.1 µm	Polycarbonate	Chemical solution	[79]
41	Polypyrrole nanotubes	РЕТ	Chemical solution	[80]



Fig.11. General scheme of electrochemical deposition of metal nanowires inside the pores of a track-etched membrane. (Reproduced from Ref. [37]).

is determined by the current density and deposition time, while the diameter of the nanowire is determined by the pore diameter of the template. After nanowires have been electrodeposited, the conducting film used for the electrochemical deposition as well as the template are then subsequently dissolved using appropriate acids or bases.

The scanning electron micrograph in Fig.12 shows the very smooth surface and uniform diameter of template made gold nanowires with diameters of 160 and 25 nm.



Fig.12. (A) SEM micrographs of 160 nm diameter gold wires; inset: end section of wires. (B) High-resolution scanning electron micrograph (HRSEM) of a 25 nm wire. (Reproduced from Ref. [46]).



Fig.13. The scheme of electrophoretic deposition process. (Reproduced from Ref. [55]).

Electrophoretic deposition can be used in the case of non-conducting material deposition such as metal oxides. Nano-sized particles required for deposition can be prepared by sol-gel method. Using the sol-gel method, making monodisperse sol with particle dimensions in the range of 1 to 100 nm and easily controlled stoichiometry is possible. In a polar solvent or an electrolyte solution with proper conditions (zeta potential value), the surface of a nanoparticle develops an electrical charge preventing its agglomeration. Under the action of an external electric field, charged particles are set in motion, as schematically illustrated in Fig.13. When hitting an electrode, the electrostatic double layers present on the particle surfaces collapse and particles coagulate, forming a porous material of compacted particles [53]. A porous template is used to restrict the deposition to occur inside the pores only. Since monoliths grown by electrophoretic deposition are porous, post-deposition sintering at elevated temperatures is usually required to form a dense material. If the initial solid particles were amorphous, sintering would also induce crystallization. A variety of materials, such as TiO₂, SiO₂, BaTiO₃, PZT, and Sr₂Nb₂O₇, have

been deposited by a combination of electrophoresis and the sol-gel method (see Table 1).

The atomic layer deposition (ALD) method is a thin film deposition method based on cyclic deposition of atoms from reactive precursors in gaseous form, supplied sequentially. It can be used for arbitrary shaped substrates and enable deposition of atomic thickness layers in one cycle. The ALD method has been successfully used with the track-etched membranes for the modification of pore surface properties and for the reduction of internal pore diameters. Conformal coatings on the pore walls of track-etched membranes with TiO₂, ZrO₂, and Al₂O₃ layers have been reported (see Table 1).

Many studies on ionic transport through small diameter nanochannels have shown a strong influence of pore wall surface charge on ion transport through the pores. There is a need to modify the pore wall surface properties. Specific local channel properties such as pore diameter variations, conformation variations of pendant bonds, swelling of pore walls, polymer surface layer or surface charge density variations due to the pH changes of a solution are usually not well known. But all of them may influence ion transport. Therefore, the development of methods for surface modification in a controlled manner in order to get a surface with well-defined properties is of great value. For macromolecular sensor development, the surface inside the nanopore should be carefully prepared, since the surface charge, roughness, and/or functional groups could significantly influence the signal-to-noise ratio and the capture rate of the analytes, and they could even lead to unwanted permanent adsorption of the analytes or clogging, if not enough attention was paid. Moreover, coating with



Fig.14. SEM BSE (scanning electron microscopy with back-scattered electrons) image of the FIB milled surface showing the TiO_2 conformal coating present inside the track-etched pores of the polycarbonate membrane. (Reproduced from Ref. [59]).

insulating durable material, like ceramic oxides, will protect the host material in some filtration applications.

The ability to reduce internal pore diameters in a controlled manner at the nanometre level is of great value for sensors development, especially in the range below 10 nm. For the protein sensor development, precise control of the pore size in the nanometre range is an important challenge, since the pore size needs to be just a little larger than the protein size in order to achieve very sensitive detection. A general view of a membrane after TiO₂ conformal coating is shown in Fig.14.

Electroless metal deposition uses a redox reaction to deposit metal on an object without the passage of an electric current, but using a plating bath. Due to its surface limitations, electroless deposition is a convenient and power saving method to produce hollow nanostructures. Most of the work on metal



Fig.15. General scheme of electroless fabrication of self-supporting nanotube network. (Reproduced from Ref. [71]).

nanotubes made electrolessly in hard and passive templates is focused on Au. However, the making of anatase titanium dioxide nanotubes (TNT) with a diameter of approximately 100 nm and a wall thickness of approximately 10 nm has been reported recently [64].

The general scheme of the electroless process of self-supported nanotubes network is shown in Fig.15.

Bilateral, open cylindrical, largely anatase titanium dioxide nanotubes with controllable diameters and wall thickness were fabricated using electroless deposition based on aqueous solutions. The TNTs have potential uses in fields like sensing, photocatalysis or regenerative energy. Using polycarbonate as a template it is possible to produce TNT arrays within the polycarbonate having a tube density of a single such that there are up to 10⁹ tubes/cm². These arrays can be directly used for sensor and photovoltaic applications.

Chemical template synthesis can be accomplished by immersing the membrane into a solution of a desired monomer and its oxidizing agent. This method can be used to make polymer nanotubes, nanowires (polypyrrole, polyaniline) as well for making metal oxide nano-sized features. Conducting polymers show preferential deposition along the walls of the polycarbonate membrane resulting in nanotubuler structures due to solvophobic interactions. These tubules close up as the deposition time is increased and eventually result in nanowires. Example of polypyrrole nanotubes is shown in Fig.16 [80].



Fig.16. SEM micrographs of polypyrrole nanotubes made in track-etched membranes with pore of diameters: $0.4 \mu m$ (A) and $1.3 \mu m$ (B).

The series of metal oxides (MgO, Cu doped ZnO, In_2O_3) for gas sensor studies have been made by moderate thermal treatment of chemically prepared precursors filling the pores in Nuclepore polycarbonate track-etched membrane (see Table 1). The crucial step was the synthesis of a suitable oximato metal complexes. After infiltration of the precursor into the pores, a two-step moder-

ate thermal treatment procedure (160°C, 450°C) was used to yield polycrystalline metal oxide rods [77-79].

3.2. USES OF TRACK-ETCHED MEMBRANES IN BIOLOGICAL RESEARCH

The achievements in the track-etching techniques, like asymmetrical nanochannel etching and chemical functionalization of nanochannel walls, give positive impetus to research and development in the field of biological applications. Fundamental to the understanding of process mechanisms in living organisms is to know the structure of ionic channels in biological membranes and the ion transport mechanisms through them. Experimental work based on the use of biological nanochannels, usually reproduced in laboratory by protein nanotubes embedded in lipid bilayers, e.g. using α -hemolysis biomolecule, has many disadvantages. These nanotubes are difficult to reproduce in practice, fragile and cannot withstand the complexity of the external environment. For experimental work, artificially made, durable nanochannels, mimicking those existing in the real biological world, would be preferable. Track-etched membranes are well-suited for this due to their biological and chemical inertness and the possibility of tuning their structural parameters by the chemical etching method. Besides nanochannels being formed with shape, diameter and length matching those found in the real biological world, pore walls can be functionalized with internal pore surface coatings, with a thin gold layer, and/or by covalent attachment of functional molecules or macromolecules, which are most important.

Thanks to the systematic studies of ionic flows in nanochannels and on the behaviour of molecules/macromolecules in confined space, it is possible to use artificial nanochannels mimicking those existing in real biological world. The main goal of this work was to quantitatively understand the fundamental laws governing the ionic and molecular transport through nanochannels, as well as to develop nanoscale devices for controlling and sensing biologically important macromolecules [20-24].

Pioneering research work [16, 17] conducted on artificial track-etched nanochannels confirmed that the ions flow through them and show features similar to these observed in biological nanochannels. These features included selectivity in ionic species transport, current fluctuations between high and low conducting state, and inhibition of ion flow by low pH and divalent cations. The encouraging results of the first experiments stimulated much broader interest and initiated more detailed research works conducted mostly by Martin's [18, 22] and Siwy's [22, 23] groups as well as work conducted at GSI Darmstadt [19, 20]. The next important step in development of artificial nanochannels, as the chemical functionalization of pore wall, has been done. The

first work conducted by Martin's group was based on using electroless conformal coating to coat pore walls with gold and on attaching to the deposited layer thiol functionalized molecules. Soon, direct functionalization methods based on using native carboxylic groups remaining on the pore walls after chemical etching for chemical reactions with molecules possessing adequate functional groups, was developed. Thus, controlled manipulation of charge density on the pore wall became possible, opening the way to the modification of transport properties of small diameter nanochannels, particularly their selectivity for cationic and anionic species.

Generally, the pore wall functionalization process is based on the attachment of molecules or macromolecules having different functional properties. In the case of molecules with polar functional groups, the charge state can be pH-dependant. Thus, the effective charge of the pore wall can be changed by changing pH. In the case of macromolecule attachment, the conformational state properties depend on external factors, like pH, temperature, UV irradiation, salt ionic strength *etc.*, and it is then possible to change the "effective diameter" of a nanochannel used for the ionic transport. Since the detection methods of pore transport are usually based on measurements of full ion--voltage characteristics, including both possible polarization directions, any partial or complete blockage of the pore wall can be detected.

Up to now, different strategies have been employed for making artificial nanochannels mimicking biological ones. These methods have been developed using polymer track-etched techniques as well as different surface functionalization methods. They can be classified into four groups:

- designing a pore with asymmetric geometry and homogeneously charged inner surface;
- designing the cylindrical pore with inhomogeneously charged surface, particularly containing two segments with different electrical properties;
- designing the pore covered with a conducting metallic layer, enabling the control of the current flow through the pore by external voltage bias;
- designing the pore with electrochemical gating, containing attached single strand of DNA in the pore.

The molecular transport in nanochannels is a complex process requiring a detailed description of the interaction of mobile ions and fixed charges on the channel surface. Usually the detailed interpretation of experimental results requires solving the coupled charge and mass balance equation – the coupled Poisson-Planck-Navier-Stocks calculation of charge and mass fluxes. Surface charges on the pore wall in the presence of an electrolyte are screened by counter-ions. The detailed ion transport properties of the channel depend strongly on the relation of so-called Debye length describing the concentration dependant charge screening process to the diameter of the nanochannels. Generally, the surface charge on the pore wall influences the ion fluxes in the narrow channels and, in the case of a weak electrolyte, influence ionic strength as



Fig.17. (A) Immobilization of functional molecules onto the inner wall of a nanochannel by electroless modification with Au and surface chemisorbing thiols. (B) A typical thiol self-assembled functional molecules for modifying the inner surface of a polymer/Au nanochannel (B). (Reproduced from Ref. [81]).

well. Detailed analyses of the ionic fluxes require solving differential equations describing charge and mass balance, the coupled Poisson-Planck-Navier-Stocks equations.

Figure 17 shows the general scheme of functionalization of pores walls of a track-etched membrane. The coating of pore walls with gold film by electroless deposition enables covalent linking of thiol-ended molecules of different lengths and functionalities using self-assembly mechanisms of the thiol-ended molecules on gold surfaces.

REFERENCES

[1]. Spohr, R. (1990). *Ions tracks and microtechnology. Principles and application*. Braunschweig: Friedr. Vieweg&Sohn Verlagsgesellschaft mbH.

- [2]. Apel, P.Y. (2013). Track-etching. In *Encyclopedia of membrane science and technology* (pp. 332-356). Wiley.
- [3]. Fink, D. (Ed.). (2014). *Fundamentals of ion-irradiated polymers*. Berlin, Heidelberg: Springer-Verlag. (Springer Series in Materials Science, Vol. 63).
- [4]. Apel, P.Y., & Fink, D. (2004). Ion-track etching. In D. Fink (Ed.), *Transport* processes in ion irradiated polymers (pp. 147-202). Springer.
- [5]. Young, D.A. (1958). Etching of radiation damage in lithium fluoride. *Nature*, *182*, 375-377.
- [6]. Price, P.B, & Walker, R.M. (1967). *The molecular sieves and methods for producing same*. US Patent No. 3,303,085.
- [7]. Fleischer, R.L., & Price, P.B. (1963). Tracks of charged particles in high polymers. *Science*, 140, 1221-1222.
- [8]. Kohli, P., & Martin, C.R. (2006). Smart nanotubes for biotechnology. *Curr. Pharm. Biotechnol.*, 6, 35-47.
- [9]. Vereshchagina, E., Mc Glade, D., Glynn, M., & Ducrée, J. (2013). A hybrid microfluidic platform for cell-based assays via diffusive and convective transmembrane perfusion. *Biomicrofluidics*, 7, 034101. DOI: 10.1063/1.4804250.
- [10]. Hulteen, J.C., & Martin, C.R. (1997). A general template-based method for the preparation of nanomaterials. J. Mater. Chem., 7(7), 1075-1087.
- [11]. Shang, H. (M.), & Cao, G. (2010). Template-based synthesis of nanorod or nanowire arrays. In Bharat Bhushan (Ed.), *Springer handbook of nanotechnol*ogy (3rd ed., pp. 169-186). Springer.
- [12]. Cao, G., & Liu, D. (2008). Template-based synthesis of nanorod, nanowire, and nanotube arrays. Adv. Colloid Interface Sci., 136, 45-64.
- [13]. Martin, C.M. (1996). Membrane-based synthesis of nanomaterials. Chem. Mater., 8, 1739-1746.
- [14]. Ferain, E., & Legras, R. (2003). Track-etch templates designed for micro- and nanofabrication. Nucl. Instrum. Meth. Phys. Res. B, 208, 115-122.
- [15]. Kuchibhatla, S.V.N.T., Karakoti, A.S., Vera, D., & Seal, S. (2007). One dimensional nanostructured materials. *Prog. Mater. Sci.*, 52(5), 699-913.
- [16]. Bashford, L. (1995). Membrane pores from biology to track-etched membranes. *Bioscience Rep.*, 15, 553.
- [17]. Pasternak, C.A., Alder, G.M., Apel, P.Yu., Bashford, C.L., Edmonds, D.T., Korchev, Y.E., Lev, A.A., Lowe, G., Milovanovich, M., Pitt, C.W., Rostovtseva, T.K., & Zhitariuk, N.I. (1995). Nuclear track-etched filters as model pores for biological membranes. *Radiat. Meas.*, 25, 675-683.
- [18]. Apel, P.Yu., Blonskaya, I.V., Dmitriev, S.N., Orelovich, O.L., & Sartowska, B.A. (2015). Ion track symmetric and asymmetric nanopores in polyethylene terephthalate foils for versatile applications. *Nucl. Instrum. Meth. Phys. Res. B*, 365, 409-413.
- [19]. Ali, M., Ramirez, P., Nguyen, H.Q., Nasir, S., Cervera, J., Mafe, S., & Ensinger, W. (2012). Single cigar-shaped nanopores functionalized with amphoteric amino acid chains: Experimental and theoretical characterization. ACS Nano, 6, 3631-3640.
- [20]. Ali, M., Neumann, R, & Ensinger, W. (2010). Sequence-specific recognition of DNA oligomer using peptide nucleic acid (PNA)-modified synthetic ion chan-

nels: PNA/DNA hybridization in nanoconfined environment. *ACS Nano*, *4*, 7267-7274. DOI: 10.1021/nn102119q.

- [21]. Zhang, H., Tian, Y, & Jiang, L. (2013). From symmetric to asymmetric design of bio-inspired smart single nanochannels. *Chem. Commun.*, 49, 10048-10063. DOI: 10.1039/c3cc45526b.
- [22]. Siwy, Z., & Martin, C. (2007). Tuning ion current rectification in synthetic nanotubes in controlled nanoscale motion. In H. Linke & A. Månsson (Eds.), *Controlled nanoscale motion. Nobel Symposium 131* (pp. 349-366). Berlin, Heidelberg: Springer. (Lecture Notes in Physics 711). DOI: 10.1007/b11823292.
- [23]. Siwy, Z., & Howorka, S. (2010). Engineered voltage-responsive nanopores. *Chem. Soc. Rev.*, 39, 1115.
- [24]. Hou, X., Zhang, H., & Jiang, L. (2012). Building bio-inspired artificial functional nanochannels: From symmetric to asymmetric modification. *Angew. Chem. Int. Ed.*, 51, 5296-5307. DOI: 10.1002/anie.201104904.
- [25]. Watt, F., Bettiol, A.A., Van Kan, J.A., Teo, E.J., & Breese, M.B.H. (2005). Ion beam litography and nanofabrication: A review. *Int. J. Nanosci.*, 4, 269-286.
- [26]. Fink, D., Alegaonkar, S., Petrov, A.V., Wilhelm, M., Szimkowiak, P., Behar, M., Sinha, D., Fahrner, W.R., Hoppe, K., & Chadderton, L.T. (2005). High energy ion beam irradiation of polymers, for electronic applications. *Nucl. Instrum. Meth. Phys. Res. B*, 236, 11-20.
- [27]. Spohr, R. (2005). Status of ion track technology Prospects of single tracks. *Radiat. Meas.*, 40, 191-202.
- [28]. Apel, P.Yu., Ivanov, O.M., Lizunov, N.E., Mamonova, T.I., Nechaev, A.N., Olejniczak, K., Vacik, J., & Dmitriev, S.N. (2015). Production of multi-, oligoand single-pore membranes using a continuous ion beam. *Nucl. Instrum. Meth. Phys. Res. B*, 365, 641-645.
- [29]. Ziegler, J.F. *SRIM The Stopping and Range of Ions in Matter. SRIM-2013*. Retrieved May 16, 2016, from www.srim.org.
- [30]. Trautmann, C., Bouffard, S., & Spohr, R. (1996). Etching threshold for ion tracks in polyimide. *Nucl. Instrum. Meth. Phys. Res. B*, *116*, 429-433.
- [31]. Vilensky, A.I., Zagorski, D.L., Kabanov, V.Ya., & Mchedlishvili, B.V. (2003). UV- and γ-sensitization of latent tracks in polyethylene terephthalate. *Radiat. Meas.*, 36, 131-135.
- [32]. Apel, P.Yu., Blonskaya, I.V., Orelovitch, O.L., Root, D., Vutsadakis, V., & Dmitriev, S.N. (2003). Effect of nanosized surfactant molecules on the etching of ion tracks: New degree's of freedom in design of pore shape. *Nucl. Instrum. Meth. Phys. Res. B*, 209, 329-334.
- [33]. Apel, P.Yu., Blonskaya, I.V., Orelovitch, O.L., Ramirez, P., & Sartowska, B.A. (2011). Effect of nanopore geometry on ion current rectification. *Nanotechnol*ogy, 22, 175302. DOI: 10.1088/0957-4484/22/17/175302.
- [34]. Zhang, Y., Kolmakov, A., Chretien, S., Metiu, H., & Moskovits, M. (2004). Control of catalytic reactions at the surface of a metal oxide nanowire by manipulating electron density inside it. *Nano Lett.*, 4(3), 403-407.
- [35]. Carretero-Genevriera, A., & Mestresb, N. (2015). Growth of 1-D oxide nanostructures. In *Encyclopedia of nanotechnology*. Dordrecht: Springer Science+Business Media. DOI 10.1007/978-94-007-6178-0_101005-1.

- [36]. Kolmakov, A., & Moskovits, M. (2004). Chemical sensing and catalysis by onedimensional metal-oxide nanostructures. *Annu. Rev. Mater. Res.*, 34, 151-180.
- [37]. Wanekaya, A.K., Chen, W., Myung, N.V., & Mulchandani, A. (2006). Nanowire--based electrochemical biosensors. *Electroanalysis*, 18, 6, 533-550.
- [38]. Stortini, A.M., Moretto, L.M., Mardegan, A., Ongaro, M., & Ugo, P. (2015). Arrays of copper nanowire electrodes: Preparation, characterization and application as nitrate sensor. *Sensor. Actuat. B-Chem.*, 207, 186-192.
- [39]. University of Florida (2016, July 12). *Martin Research Group*. Retrieved July 16, 2016 from https://martin.chem.ufl.edu/.
- [40]. Walewyns, T., Scheena, G., Tootena, E., & Francis, L.A. (2011). Synthesis of patterned freestanding nickel nanowires by using ion track-etched polyimide. In Á.B. Rodríguez-Vázquez, R.A. Carmona-Galán, G. Liñán-Cembrano, R. Adelung & C. Ronning (Eds.), *Bioelectronics, Biomedical, and Bioinspired Systems V; and Nanotechnology V*. (Proc. SPIE, Vol. 8068). DOI: 10.1117/12.886775.
- [41]. Chtanko, N., Toimil Molares, M.E., Cornelius, T., Dobrev, D., & Neumann, R. (2004). Etched single-ion-track templates for single nanowire synthesis. J. Phys. Chem. B, 108, 9950-9954.
- [42]. Schönenberger, C., van der Zande, B.M.I., Fokkink, L.G.J., Henny, M., Schmid, C., Krüger, M., Bachtold, A., Huber, R., Birk, H., & Staufer, U. (1997). Template synthesis of nanowires in porous polycarbonate membranes: Electrochemistry and morphology. J. Phys. Chem. B, 101, 5497-5505. DOI: 10.1021/jp963938g.
- [43]. Ferain, E., & Legras, R. (2009). Templates for engineered nano-objects for use in microwave, electronic devices and biomedical sensing application. *Nucl. Instrum. Meth. Phys. Res. B*, 267, 1028-1031.
- [44]. Enculescu, I., Siwy, Z., Dobrev, D., Trautmann, C., Toimil Molares, M.E., Neumann, R., Hjort, K., Westerberg, L., & Spohr, R. (2003). Copper nanowires electrodeposited in etched single-ion track templates. *Appl. Phys. A*, 77, 751-755.
- [45]. Ravish Garg, Samiksha Mehta, Amandeep Kaur, & Chauhan, R.P. (2012). Template based synthesis of low dimensional structures of copper and their characterization. *Int. J. Eng. Res. Dev.*, 3, 4, 1-4.
- [46]. Karim, S., Toimil-Molares, M.E., Maurer, F., Miehe, G., Ensinger, W., Liu, J., Cornelius, T.W., & Neumann, R. (2006). Synthesis of gold nanowires with controlled crystallographic characteristics. *Appl. Phys. A*, 84, 403-407.
- [47]. Ensinger, W. (2007). Formation of nanopore membranes and nanowires by high energy ion irradiation of polymer foils. *Surf. Coat. Technol.*, 201, 8442-8447.
- [48]. Karima, S., Ensinger, W., Mujahid, S.A., Maaz, K., & Khan, E.U. (2009). Effect of etching conditions on pore shape in etched ion-track polycarbonate membranes. *Radiat. Meas.*, 44, 9-10, 779-782.
- [49]. Tian, M., Wang, J., Kurtz, J., Mallouk, Th.E., & Chan, M.H.W. (2003). Electrochemical growth of single-crystal metal nanowires via a two-dimensional nucleation and growth mechanism. *Nano Lett.*, 3, 7, 919-923.
- [50]. Toimil-Molares, M.E. (2012). Characterization and properties of micro- and nanowires of controlled size, composition, and geometry fabricated by electrodeposition and ion-track technology. *Beilstein J. Nanotechnol.*, 2012, 3, 860-883. DOI: 10.3762/bjnano.3.97.

- [51]. Picht, O., Müller, S., Alber, I., Rauber, M., Lensch-Falk, J., Medlin, D.L., Neumann, R., & Toimil-Molares, M.E. (2012). Tuning the geometrical and crystallographic characteristics of Bi₂Te₃ nanowires by electrodeposition in ion-track membranes. J. Phys. Chem. C, 116, 5367-5375.
- [52]. Matei, E., Preda, N., Enculescu, M., Ansermet, J.-P., Toimil Molares, M.E., & Enculescu, I. (2010). Sequential deposition of multisegment nanowires. *Dig. J. Nanomater. Biostruct.*, 5, 4, 1067.
- [53]. Limmer, S.J., Seraji, S., Forbess, M.J., Wu, Y., Chou, T.P., Nguyen, C., & Cao, G.Z. (2001). Electrophoretic growth of lead zirconate titanate nanorods. *Adv. Mater.*, 13, 16, 1269-1272.
- [54]. Limmer, S.J., & Cao, G. (2003). Sol-gel electrophoretic deposition for the growth of oxide nanorods. *Adv. Mater.*, 15, 5, 427-431.
- [55]. Limmer, S.J., Chou, T.P., & Cao, G.Z. (2005). A study on the influences of processing parameters on the growth of oxide nanorod arrays by sol electrophoretic deposition. J. Sol-Gel Sci. Technol., 36, 183-195.
- [56]. Mohammadi, M.R., Ordikhani, F., Fray, D.J., & Khomamizadeh, F. (2011). Template-based growth of titanium dioxide nanorods by a particulate sol-electrophoretic deposition process. *Particuology*, 9, 161-169.
- [57]. Sobel, N., Hess, Ch., Lukas, M., Spende, A., Stühn, B., Toimil-Molares, M.E., & Trautmann, Ch. (2015). Conformal SiO₂ coating of sub-100 nm diameter channels of polycarbonate etched ion-track channels by atomic layer deposition. *Beilstein J. Nanotechnol.*, 2015, 6, 472-479.
- [58]. Wang, C., Fu, Q., Wang, X., Kong, D., Sheng, Q., Wang, Y., Chen, Q., & Xue, J. (2015). Atomic layer deposition modified track-etched conical nanochannels for protein sensing. *Anal. Chem.*, 87, 8227-8233. DOI: 10.1021/acs.analchem.5b01501.
- [59]. Triani, G., Evans, P.J., Attard, D.J., Prince, K.E., Bartlett, J., Tan, S., & Burford, R.P. (2006). Nanostructured TiO₂ membranes by atomic layer deposition. J. Mater. Chem., 16, 1355-1359. DOI: 10.1039/B516499K.
- [60]. Asatekin, A., & Gleason, K.K. (2011). Polymeric nanopore membranes for hydrophobicity-based separations by conformal initiated chemical vapor deposition. *Nano Lett.*, 11, 677-686.
- [61]. Chen, P., Mitsui, T., Farmer, D.B., Golovchenko, J., Gordon, R.G., & Branton, D. (2004). Atomic layer deposition to fine-tune the surface properties and diameters of fabricated nanopores. *Nano Lett.*, *4*, 1337.
- [62]. Spende, A., Sobel, N., Lukas, M., Zierold, R., Riedl, J.C., Gura, L., Schubert, I., Moreno, J.M., Nielsch, K., Stühn, B., Hess, C., Trautmann, C., & Toimil-Molares, M.E. (2015). TiO₂, SiO₂, and Al₂O₃ coated nanopores and nanotubes produced by ALD in etched ion track membranes for transport measurements. *Nanotechnology*, 26, 335301. DOI: 10.1088/0957-4484/26/33/335301.
- [63]. Velleman, L., Shapter, J.G., & Losic, D. (2013). Gold nanotube membranes. In E.M.V. Hoek & V.V. Tarabara (Eds.), *Encyclopedia of membrane science and technology* (pp. 1-27). John Wiley & Sons, Inc. DOI: 10.1002/9781118522318.
- [64]. Boehme, M., Fu, G., Ionescu, E., & Ensinger, W. (2010). Fabrication of anatase titanium dioxide nanotubes by electroless deposition using polycarbonate for separate casting method. *Nano-Micro Lett.*, 2, 26-30. DOI: 10.1007/BF03353613.

- [65]. Muench, F., Kaserer, S., Kunz, U., Svoboda, I., Brotz, J., Lauterbach, S., Kleebe, H.-J., Roth, Ch., & Ensinger, W. (2011). Electroless synthesis of platinum and platinum-ruthenium nanotubes and their application in methanol oxidation. J. Mater. Chem., 21, 6286-6291.
- [66]. Muench, F., Oezaslan, M., Rauber, M., Kaserer, S., Fuchs, A., Mankel, E., Brötz, J., Strasser, P., Roth, Ch., & Ensinger, W. (2013). Electroless synthesis of nano-structured nickel and nickel boron tubes and their performance as unsupported ethanol electrooxidation catalysts. *J. Power Sources*, 222, 243-252.
- [67]. Muench, F. (2014). Polycarbonate activation for electroless plating by dimethylaminoborane absorption and subsequent nanoparticle deposition. *Appl. Phys. A*, *116*, 287-294.
- [68]. Gasparac, R., Taft, B.J., Lapierre-Devlin, M.A., Lazareck, A.D., Xu, J.M., & Kelley, S.O. (2004). Ultrasensitive electrocatalytic DNA detection at two- and three-dimensional nanoelectrodes. J. Am. Chem. Soc., 126, 12270-12271.
- [69]. Felix, E.M., Antoni, M., Pause, I., Schaefer, S. Kunz, U., Weidler, N., Muench, F., & Ensinger, W. (2016). Template-based synthesis of metallic Pd nanotubes by electroless deposition and their use as catalysts in the 4-nitrophenol model reaction. *Green Chem.*, 18, 558-564.
- [70]. Lapierre-Devlin, M.A., Asher, C.L., Taft, B.J., Gasparac, R., Roberts, M.A., & Kelley, S.O. (2005). Amplified electrocatalysis at DNA-modified nanowires. *Nano Lett.*, 5, 6, 1051-1055.
- [71]. Muench, F., De Carolis, D.M., Felix, E.-M., Brötz, J., Kunz, U., Kleebe, H.-J., Ayata, S., Trautmann, Ch., & Ensinger, W. (2015). Self-supporting metal nanotube networks obtained by highly conformal electroless plating. *ChemPlusChem*, 80, 1448-1456.
- [72]. Velleman, L., Shapter, J.G., & Losic, D. (2009). Gold nanotube membranes functionalised with fluorinated thiols for selective molecular transport. J. *Membr. Sci.*, 328, 121-126.
- [73]. Muench, F., Oezaslan, M., Seidl, T., Lauterbach, S., Strasser, P., Kleebe, H.-J., & Ensinger, W. (2011). Multiple activation of ion track etched polycarbonate for the electroless synthesis of metal nanotubes. *Appl. Phys. A*, 105, 847-854.
- [74]. Enculescu, I., Sima, M., Enculescu, M., Matei, E., Toimil Molares, M.E., & Cornelius, Th. (2008). Nickel nanotubes prepared by electroless deposition in ion track templates. *Optoelectron. Adv. Mat.*, 2, 3, 133-136.
- [75]. Shao, P. (2005). Gold nanotube membranes: Preparation, characterization and application for enantioseparation. *J. Membr. Sci.*, 255, 1-11.
- [76]. Kumar, V., Singh, R., & Chakarvarti, S.K. (2007). Novel electroless template based synthesis of silver microtubules and their characterization. *Dig. J. Nanomater. Biostruct.*, 2, 1, 163-167.
- [77]. Pashchanka, M., Hoffmann, R.C., Gurlo, A., Swarbrick, J.C., Khanderi, J., Engstler, J., Issanin, A., & Schneider, J.J. (2011). A molecular approach to Cu doped ZnO nanorods with tunable dopant content. *Dalton Trans.*, 40, 4307.
- [78]. Pashchanka, M., Hoffmann, R.C., & Schneider, J.J. (2010). Controlled synthesis and characterisation of MgO nanoparticles, thin films and polycrystalline nanorods derived from a Mg(II) single source precursor. J. Mater. Chem., 20, 957-963.

- [79]. Pashchanka, M., Hoffmann, R.C., Gurlo, A., & Schneider, J.J. (2010). Molecular based, chimie douce approach to 0D and 1D indium oxide nanostructures. Evaluation of their sensing properties towards CO and H₂. J. Mater. Chem., 20, 8311-8319.
- [80]. Starosta, W., Buczkowski, M., Sartowska, B., & Wawszczak, D. (2006). Studies on template-synthesized polypyrrole nanostructures. *Nukleonika*, 51, Suppl. 1, S35-S39.
- [81]. Xu Hou, Huacheng Zhang, Lei Jiang, (2012). Nanochannels: From symmetric to asymmetric modification. *Angew. Chem. Int. Ed.*, *51*, 5296-5307.