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SYNTHESIS OF POLYMERIC MICRO- AND
NANOSTRUCTURAL MATERIALS FOR APPLICATION
IN NONLINEAR OPTICS

33a

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INTRODUCTION

Interest has grown essentially recently to the problem of producing micro- and nanostructural materials with the use of porous materials as a template [1, 2]. The essence of the method consists in filling the pores of the template by a desired material with the help of various physicochemical methods. These investigations are of a major practical and scientific importance, as they allow one to gain a wide spectrum of micro- and nanostructural materials with unique properties which find their application in many areas of modern science and technologies — nanoelectronics, photonics, chemotronics, biotechnologies, etc. Two types of porous membranes, the aluminum membranes and polymeric track membranes are often used as templates. Aluminum membranes are received via anodization of aluminum foil in an acid media [3], and track membranes are produced by irradiation of polymeric films with a beam of high energy heavy ions, followed by a subsequent chemical etching of latent tracks of these particles [4, 5]. Both types of membranes have cylindrical pores with a narrow distribution along the diameter that gives an opportunity for synthesis of micro- and nanostructural objects — wires, tubules as well as composite membranes. In case the pore area is completely filled by the desired material, micro- and nanowires are produced. If the used material is deposited only on the pore walls, micro- and nanotubules are formed. In order to filling the pores of template, various materials can be used: metals [6–8], carbon [9, 10], semiconductors [11, 12], polymers [13–15]. The micro- and nanostructures can remain inside the pores of the template or they can be freed from membrane. To produce micro- and nanowires as well as micro- and nanotubules as an ensemble of free particles, one dissolves porous matrix by a suitable solvent, and then they can be collected on a substrate after filtration. If the nanostructural objects (wires or tubules) are attached to a surface of the substrate and the membrane is removed, an ensemble of structures like the bristles of a brush can be obtained. Synthesized micro- and nanotubules can be left inside the pores of template, the composite micro- and nanomembranes are produced in this case the properties of which can vary under the influence of external factors, such as solution pH, electric current, ionic force of the solution [16–18].

One of the directions in the micro- and nanostructures creation with using the porous membranes as templates is electrolytic deposition. This method is used for the synthesis of micro- and nanowires as well as micro- and nanotubules from

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metals. Another direction is related to the chemical or electrochemical polymerization of monomers. This direction looks more promising as it allows one to use a wide assortment of organic compounds and to obtain composite micro- and nanostructural materials that often possess unique properties. Among them the polymers with electric conducting properties are of special significance [19–21]. In line with the traditional methods of producing micro- and nanostructural materials by the template method, for the last few years the method of obtaining nanomembranes by polymerization of monomer vapors in plasma has been used more and more often [22, 23]. In our opinion, the use of plasma has a number of advantages, namely, a possibility of regulating the thickness and density of the polymeric layer. It also provides its high adhesion to the pattern and allows one to reduce the duration of the synthesis and to use a wider spectrum of organic compounds, for which the standard polymerization is excluded. Selection of the method of forming the micro- and nanostructural materials is determined by the nature of the chemical compound used.

This paper describes a new approach developed for obtaining of micro- and nanostructural materials (wires and tubules as well as composite membranes) on the basis of polymeric compositions used as matrix for application in nonlinear optics. This approach consists in filling the pores of the template by the polymers. As a template for synthesis of micro- and nanostructural materials, the developed and serially produced at the Flerov Laboratory of Nuclear Reactions of the Joint Institute for Nuclear Research track membranes on the basis of poly(ethylene terephthalate) (PET TM) were used. Studying the mechanism of formation of these materials as well as the research of their structure and properties were performed. As a polymer for filling the template pores, the polymeric compositions on the basis of styrene, butylmethacrylate and 4-aminostyrene were used. An impregnation method was applied for obtaining the polymeric micro- and nanostructural materials. The developed method of producing micro- and nanostructural materials provides a possible way of creation of polymeric objects with nonlinear optical properties which can be used for designing electronic micro- and nanodevices and for obtaining chemical and optical sensors.

EXPERIMENTAL

As a template for synthesis of micro- and nanostructural materials, the PET track membranes with the thickness of $10.8 \mu\text{m}$ and an effective pore diameter of $1.0 \mu\text{m}$ (pore density was $1.5 \cdot 10^7 \text{ cm}^{-2}$) as well as with the thickness of $19.8 \mu\text{m}$ and an effective pore diameter of $3.0 \mu\text{m}$ (pore density was $1.0 \cdot 10^6 \text{ cm}^{-2}$) were used. In order to produce the membranes, poly(ethylene terephthalate) films were irradiated by krypton positive ions, accelerated to the energy $\sim 3 \text{ MeV/nucleon}$ at the cyclotron, and then subjected to physicochemical treatment using the technique

[5]. As a precursor for obtain of micro- and nanostructural materials the polymeric compositions were used. These polymeric compositions were obtained by radical copolymerization of styrene and butylmethacrylate (in ratio of 50:50 mol %) and styrene, butylmethacrylate and 4-aminostyrene (in ratio of 20:50:30 mol %) as described in [24]. Toluene was used to dissolve the polymeric compositions. The concentration of the polymeric compositions in the solvent was varied from 0.5 to 20%. The membranes were covered by a solution of polymeric compositions with the help of an impregnation device of «meniscus» type (see the scheme in Fig. 1).

The essence of the technique of drawing the polymeric compositions on the surface of membranes consisted in the following. The membrane, as a flexible basis, is fixed on a rotating drum of a diameter of 50 cm. The drum begins its movement with the help of reversible engine. The bath with a solution of the polymeric composition is placed on a horizontal small table under the drum. As far as the bath approaches the drum, the solution is uniformly distributed over the membrane surface and then the solvent is subjected to evaporation at room temperature. Full drying of the samples was carried out in the clean (free of dust) chamber at elevated temperature.

The characteristics of the initial membrane and membranes with a deposited layer of the polymeric compositions were determined through a series of complementary procedures. The amount of the polymeric composition on the membrane surface, defined by relation

$$Q_g = (m_g - m_o)100/m_o,$$

where m_o is the mass of initial membrane and m_g is the mass of membrane with the layer of polymeric composition. The change of the membrane thickness was measured with an electron counter of thickness «Tesa Unit» (Austria), the precision of the measuring being $\pm 0.1 \mu\text{m}$. The gas flow rate through the membranes — a flow of gas (air) passing the membrane with a square in 1 cm^2 was defined at a pressure drop of 10^4 Pa . Gas consumption was measured by float-type flow meter. On the basis of the values obtained according to these experiments, the gas-dynamical pore diameter (an effective pore diameter) was determined, as described in [25]. The changing of the surface properties of the membranes was conducted by measuring the contact angle. For this purpose the sessile drop method by using a horizontal microscope equipped with a goniometer was applied. Water (doubly distilled) was used as a test liquid. Six measurements

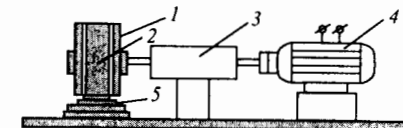


Fig. 1. Scheme of the impregnation device: 1 – drum; 2 – membrane; 3 – reducer; 4 – reversible engine; 5 – bath with solution of polymeric composition

were made at different places on the membrane surface and averaged. The study of the samples microstructure as well as the determination of the pore diameter on the membrane surface was conducted by SEM using the JSM-840 (JEOL). Before scanning, a thin layer of gold was deposited using JEOL JFC-1100 ion sputter. In order to get a clear fracture of the membrane samples, they were preliminary exposed to UV-radiation to destroy the initial polymer matrix [26].

RESULTS AND DISCUSSION

Research on the process of synthesis of the micro- and nanostructural materials by the impregnation method with use of TM as template has shown that for both types of membranes with increasing concentration of the polymeric compositions in the solvent one observes a gradual growth in the mass of the samples (Table 1) connected with formation of a polymeric layer on their surface. Moreover, while increasing the sample weight, one can observe increase in the thickness of the membranes and decrease of their effective pore diameter. This means that the formation of the polymer occurs both on the membrane surface and on the pore walls. The essential reduction (up to 100%) of the effective pore

Table 1. Change of the membrane characteristics during a process of template synthesis

Concentration of polymeric composition* in solvent, %	Relative increase in the mass, %	Thickness, μm	Relative increase in the thickness, %	Air flow rate at $\Delta P = 10^4 \text{ MPa}$, $\text{ml/min}\cdot\text{cm}^2$	Effective pore diameter, μm	Relative decrease in the effective pore diameter, %
Control	–	10.8	–	3200	1.00	–
0.5	1.7	10.8	0.50	965	0.74	26.0
1.0	2.4	10.9	0.95	525	0.62	38.0
2.0	3.6	11.0	1.85	185	0.47	54.0
2.5	4.0	11.1	2.75	90	0.38	63.2
Control	–	19.8	–	6600	3.00	–
2.0	1.8	20.0	1.0	4650	2.70	7.2
5.0	4.3	20.2	2.0	1200	1.90	38.4
10.0	7.4	20.4	3.0	180	1.15	60.3
15.0	9.4	20.6	4.0	0	0	100

* The polymeric composition of styrene and butylmethacrylate in ratio of 50:50 mol % was used in these experiments.

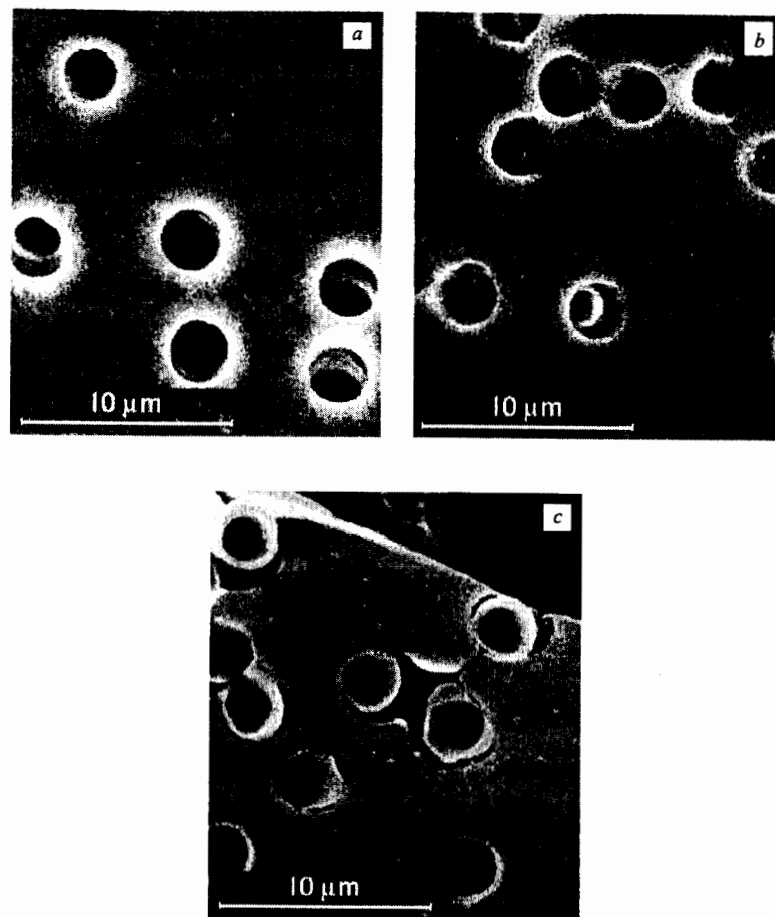


Fig. 2. SEM images of the surface of the initial membrane with a pore diameter of $3.0 \mu\text{m}$ (a), with layer of a polymeric composition of styrene and butylmethacrylate in ratio of 50:50 mol % (b) and after deformation of layer of polymeric composition (c). Concentration of polymeric composition in a solvent was 2%

diameter of the membranes in comparison with insignificant increase (up to 4%) in their thickness allows one to make a conclusion that the formation of the polymer inside the pores prevails its formation on the membrane surface. At small concentration of the polymeric compositions in the solvent, the pore diameter on the membrane surface, determined with the help of electron microscopy, practically does not differ from the pore diameter on the surface of the initial membrane (Fig. 2, b). Besides, the research of the cross sections of these membranes shows

that the formation of the polymer on the pore surface occurs uniformly. It means that the formed composite membranes have cylindrical pores, the cross section of which does not change along the whole channel. In other words, in case of using low concentrations of polymeric compositions in the solution, a formation of tubular membranes takes place. The structure of such membranes is preserved. A nominal pore diameter of the membranes of such a type is determined by the size of the pore diameter on their surface. It is obvious that the choice of concentration of a polymeric composition in the solvent at formation of tubular membranes is determined by the pore diameter of the initial membrane. So, for PET TM with a pore diameter of $1.0 \mu\text{m}$, the formation of membranes of this type occurs if using concentration of the polymeric compositions in a range from 0.5 up to 1.0%. For PET TM with a pore diameter of $3.0 \mu\text{m}$, the formation of tubular membranes is observed if the concentration of the polymeric compositions is in the range from 2.0 up to 5.0%.

Research in the surface properties of tubular membranes shows that formation of polymers from a mixture of monomers selected for the research leads to hydrophobization of the membrane surface — the water contact angle (Θ) for all membranes raises. So, if for initial PET TM $\Theta = 65^\circ$, then for treated membranes the value of water contact angle, irrespective of the concentration of the polymeric compositions in the solvent, is $80\text{--}82^\circ$ in case using copolymer of styrene and butylmethacrylate and is 95° in case using terpolymer of styrene, butylmethacrylate and 4-aminostyrene. The identical values of water contact angle in both cases for all modified membranes allow us to conclude that the polymeric compositions, even at low concentration in the solvent, completely cover the membrane surface and they uniformly distribute over the membrane surface. The particular value of the water contact angle of the membrane surface is determined by the properties of the polymeric compositions whose chemical structures can be expressed in the case of double copolymer from styrene and butylmethacrylate by the formula given in Fig. 3, *a* and in the case of terpolymer from styrene, butylmethacrylate and 4-aminostyrene by the formula given in Fig. 3, *b*.

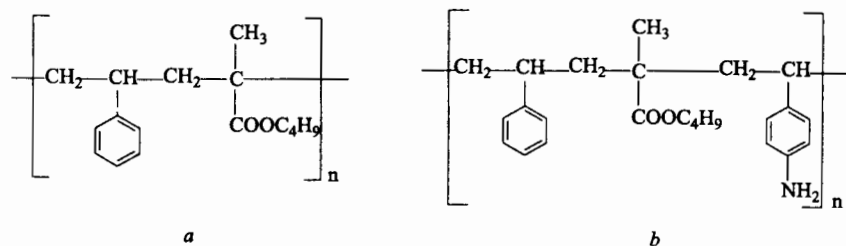


Fig. 3. Chemical structures of copolymer from styrene and butylmethacrylate (*a*) and terpolymer from styrene, butylmethacrylate and 4-aminostyrene (*b*)

The formation of the polymer on the surface of the initial membrane with more clear hydrophobic characteristics is seen also from the results of the analysis of characteristic X-ray radiation performed with the help of electron microscopy. So, according to experimental data (Table 2), the content of oxygen decreases

Table 2. Change of relative content of oxygen to carbon atoms during a process of treatment by solution of polymeric composition from styrene and butylmethacrylate

Membrane sample	Initial PET TM	PET TM treated by solution of of polymeric composition with concentration of			
		0.5%	1.0%	2.0%	2.5%
Relative content of oxygen to carbon atoms, %	39.0*	35.8	35.3	34.9	34.6

*The calculated value of content of oxygen to carbon atoms is 40%.

in the membranes modified by the solutions of polymer composites formed from copolymer of styrene and butylmethacrylate. In this case, the thicker the layer of the polymer composite on the membrane surface, the more noticeable decrease of the oxygen content in the membrane matrix is observed.

At increasing concentration of the polymeric compositions in solvent, one observes essential reduction of the effective pore diameter (Table 1). If so, the pore diameter on the membrane surface in some cases practically does not change. This means that the pores of such membranes are corked up on some depth from the surface. Electron microscopic research of the membrane cross sections confirms this conclusion. As is seen from the microphotographs in Fig. 4, in membrane pores upon completing the treatment by impregnation method, a layer of polymer is formed. The structure of such types of membranes in this case changes — pores get an asymmetric form. The nominal pore diameter of such membranes is determined by the pore diameter of the polymeric layer. The pore diameter of this layer is much less than pore diameter of the initial membrane and so the selectivity in the process of electrolyte separation of the produced membranes grows up, i.e., in this case, the formation of nanomembranes with a selective layer takes place. Note the concentration of the polymeric compositions in solvent essentially influences the thickness of the selective layer. As is clearly seen (Fig. 4), at increasing the concentration of polymeric composition in the solution, the thickness of the selective layer increases.

When choosing a significant concentration of the polymeric composition in solvent one observes a full corking of the pores. So, when drawing a composite mixture with concentration of 15% on the surface of initial PET TM with a pore diameter of $3.0 \mu\text{m}$, its effective pore diameter decreases down to zero. Research on the cross sections of this membrane by electron microscope shows, however,

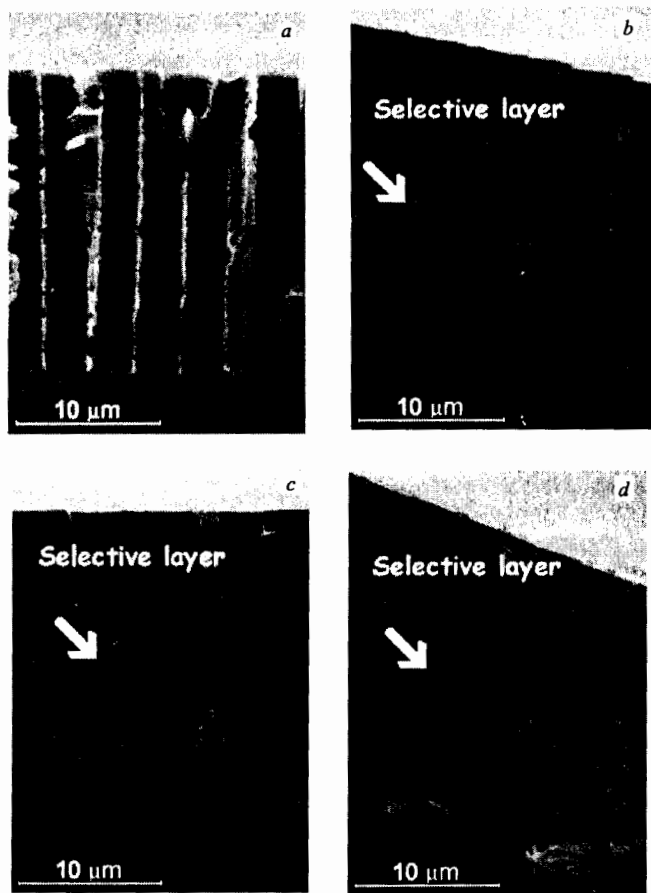


Fig. 4. SEM images of the cross sections of the initial membrane with a pore diameter of $3.0 \mu\text{m}$ (a) and composite membranes with various thickness of the selective layer. Concentration of polymeric composition from styrene and butylmethacrylate in a solvent was 5% (b), 10% (c) and 15% (d)

that in this case, a nanomembrane with a selective layer is formed (Fig. 4, d), i.e., full corking of pores occurs only in part of pore channels. The membranes of such a type can be used for gas separation.

At the further increase of the concentration of the polymeric composition in solvent, the full corking of pores occurs over all the length of pore channels. So, at drawing a composite mixture with concentration of 20% on the surface of the initial PET TM with a pore diameter of $1.0 \mu\text{m}$, as electron microscopic research shows, the pore area is completely filled by a composite polymer. Dissolution of

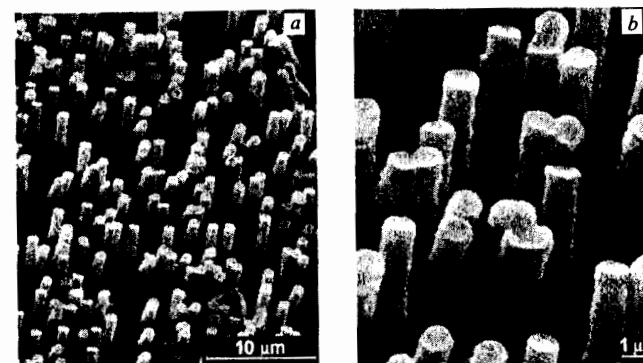


Fig. 5. SEM images of the polymeric microwires that were obtained using PET TM with a pore diameter of $1.0 \mu\text{m}$ as template. Concentration of polymeric composition from styrene, butylmethacrylate and 4-aminostyrene in a solvent was 20%

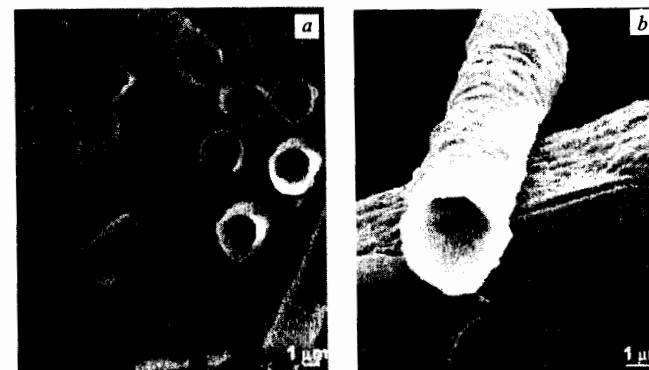


Fig. 6. SEM images of the polymeric microtubules that were obtained using PET TM with a pore diameter of $3.0 \mu\text{m}$ as template. Concentration of polymeric composition from styrene and butylmethacrylate in a solvent was 5%

the matrix of the membrane in water solution of alkali with concentration of 20% in this case leads to formation of microstructural objects — microwires (Fig. 5). The matrix of the membrane can be dissolved also in the case of formation of membranes. Its removal thus leads to formation of microtubules (Fig. 6) which then can be collected easily on the substrate after filtration.

CONCLUSION

The performed investigations have allowed us to make the following conclusions. Research on the process of formation of micro- and nanostructural materials by the impregnation method with the use of track membranes as templates has shown that depending on the concentration of polymeric compositions in the solvent it is possible to form both micro- and nanostructural materials (tubules or wires) and composite nanomembranes. To produce micro- and nanowires as well as micro- and nanotubules, the pore region of the initial membranes was filled with a polymeric composition, then the membrane matrix was dissolved in water solution of alkali, and the synthesized nanoobjects were accumulated on the substrate after filtration. In doing so, in the first case, the pore region was filled fully with polymeric composition, while in the second case, the polymeric composition was formed only on the pore walls. To obtain nanomembranes, polymeric compositions after deposition were remained inside the pores of the membranes. The research in the mechanism of forming nanomembranes shows that depending on concentration of polymeric compositions in the solvent, the formation of membranes is possible in which the deposition of the polymeric layer on the walls of the pores occurs along the all its length, as well as nanomembranes with a selective layer in which the deposition of polymeric composition occurs along a part of the pore channel.

This work only considers a method of forming the micro- and nanostructures on the basis of polymer composites that can serve as a matrix to produce micro- and nanotubules, micro- and nanowires as well as composite nanomembranes with nonlinear optical properties. In order to give the nonlinear properties to these materials, one needs to introduce to their structure the organic compounds containing chromophore groups. Such compounds can be introduced as monomers at the stage-of synthesizing copolymers used to fabricate of micro- and nanostructural materials, or else by adding to the solvent at the stage of preparing the solutions of polymeric compositions. Thus depending on chemical structure of the organic compound used, obtaining micro- and nanostructural materials with a big polarizability and with photorefractive as well as with photochromic properties is possible. We will do such a work in our future more detailed study.

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REFERENCES

1. *Martin C. R.* // Chem. Mater. 1996. V. 8. P. 1739.
2. *Hulteen J., Martin C. R.* // J. Mater. Chem. 1997. V. 7. P. 1075.

3. *Despic A., Parkhuc V. P.* Modern Aspect of Electrochemistry / Ed. by Bockris J.O., White R.E., Conway B.E. V. 20. N. Y.: Plenum Press, 1989.
4. *Ballew H. W.* Basics of Filtration and Separation. Pleasanton, CA: Nucleopore Co., 1978.
5. *Flerov G. N.* // Vestnik Akademii Nauk SSSR. 1984. V. 4. P. 35 (in Russian).
6. *Hornyak G. L., Patrissi C. J., Martin C. R.* // J. Phys. Chem. 1997. V. 101. P. 1548.
7. *Schwanbeck H., Schmidt U.* // Electrochem. Acta. 2000. V. 45. P. 4389.
8. *Wirtz M., Martin C. R.* // Adv. Mater. 2003. V. 15. P. 455.
9. *Che G., Lakshmi B. B., Martin C. R., Fisher E. R., Ruoff R. S.* // Chem. Mater. 1998. V. 8. P. 260.
10. *Abatemarco T., Stickel J., Belfort J., Frank B. P., Ajayan P. M., Belfort G.* // J. Phys. Chem. 1999. V. 103. P. 3534.
11. *Lakshmi B. B., Dorhout P. K., Martin C. R.* // Chem. Mater. 1997. V. 9. P. 857.
12. *Enculescu I., Sima M., Ghiordanescu V., Secu M.* // Chalogenide Lett. 2005. V. 2. P. 9.
13. *Dauginet-De Pra L., Ferain E., Legras R., Demoustier-Champagne S.* // Nucl. Instr. Meth. B. 2002. V. 196. P. 81.
14. *Ferain E., Legras R.* // Nucl. Instr. Meth. B. 2003. V. 208. P. 115.
15. *Cepak V. M., Martin C. R.* // Chem. Mater. 1999. V. 11. P. 1363.
16. *Kobayashi Y., Martin C. R.* // Anal. Chem. 1999. V. 71. P. 3665.
17. *Lee S. B., Martin C. R.* // Anal. Chem. 2001. V. 73. P. 768.
18. *Martin C. R., Nishizawa M., Jirage M. K., Kang M., Lee S. B.* // Adv. Mater. 2001. V. 13. P. 1351.
19. *Qiu H., Zhai J., Li S., Jiang L., Wan M.* // Adv. Func. Mater. 2003. V. 13. P. 925.
20. *Saha S. K., Su Y. K., Lin C. L., Jaw D. W.* // Nanotechnology. 2004. V. 15. P. 66.
21. *Malinauskas A., Malinauskiene J., Ramanavicius A.* // Nanotechnology. 2005. V. 16. P. 51.
22. *Kravets L., Dmitriev S., Gilman A., Drachev A., Dinescu G.* // J. Memb. Sci. 2005. V. 263. P. 127.
23. *Lazea A., Kravets L. I., Dmitriev S. N., Dinescu G.* // Romanian Rep. Phys. 2005. V. 57. P. 396.
24. *Palistrant N., Meinhard H., Grau P., Bivol V., Robu S.* // SPIE Proc. Canada. 2004. V. 5582. P. 452.
25. *Ovchinnikov V. V., Seleznev V. D.* // Izmerit. Tekhn. 1989. V. 3. P. 12.
26. *Orelovitch O. L., Apel P. Yu.* // Instr. Exp. Techn. 2001. V. 44. P. 111.

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