https://doi.org/10.18321/ectj721

Separation Efficiency of Water/Oil Mixtures by Hydrophilic and Oleophobic Membranes Based on Stainless Steel Meshes with Openings of Various Sizes

F.R. Sultanov[1,2*], Ch. Daulbayev[1,2], B. Bakbolat[1,2], Z.A. Mansurov[1,2]

[1]Al-Farabi Kazakh National University, 71 Al-Farabi ave., 050040, Almaty, Kazakhstan
[2]Institute of Combustion Problems, Bogenbay batyr str, 172, 050012, Almaty, Kazakhstan

Article info

Received:
17 January2017

Received in revised form:
24 March 2018

Accepted:
16 May 2018

Keywords:
membranes
oleophobicity
separation
mesh
dip-coating

Abstract

This article is focused on development of hydrophilic and oleophobic composition which serves as a coating for substrate presented by stainless steel meshes with different sizes of their openings. Membranes obtained by dip-coating method are hydrophilic and oleophobic and this may be applied for efficient separation of organic liquids and water by simple and inexpensive gravitational separation. Investigations presented in the article show that the size of openings of meshes influence on the formation of hydrophilicity and oleophobicity of membrane, as well as the nature of used polymers, which serve as a coating, since membranes based on 400 mesh coated with Poly(diallyldimethylammonium chloride) (PDDA)/pentadecafluorooctanoic acid (PFOA)/SiO_2 demonstrate different wettability in regard to organic liquids of different densities. In particular, membrane based on mesh 400 coated with PDDA/PFOA/SiO_2 exhibits strong oleophobicity to less dense non-polar organic solvents – kerosene, which does not penetrate the membrane, while more dense liquids, such as vacuum pump oil, are able to penetrate it, but the rate of penetration is rather slow, 10 ml per 21 min. Obtaining of membranes with uniform coating by hydrophilic-oleophobic compositions without clogging of their openings and creation of openings of required sizes for a particular case is also a subject of study of this article.

1. Introduction

Surface modification of porous materials in order to obtain specific wettability of their surfaces is of a great interest of scientists. A numerous hydrophobic and oleophilic material structures have been reported as a solution for oil/water separation [1–4]. These materials include polydimethylsiloxane-coated surfaces [5], polytetrafluoroethylene-coated materials [6], carbon based aerogels and sponges [7–10], crosslinked polymers as a gel [11–12]. High porosity as well as large BET surface area makes them excellent water-repellent sorbents with high values of sorption capacity. However, oleophilic materials have a big challenge for application due to their fouling [13–14], i.e. oil penetrates the pores and blocks them and this result in decrease of their separating ability. This oil is hard to remove and may cause secondary pollution when discarded. In addition, these materials requires some additional equipment, for example, pumps that in turn increase the energy consumption.

Discussed above challenges of superhydrophobic and oleophilic materials are moving interest to opposite in their properties, more precisely, in type of wettability, hydrophilic and oleophobic materials. When droplet of water contacts with such surface, it penetrates it completely, while organic liquids remain on its surface. This type of surface wettability generates a range of their perspective applications: anti-fogging films, self-cleaning surfaces, microfluidic devices, liquid-liquid separation membranes and anti-bioadhesion coatings [15–21]. Due to difference in density of liquids, water drops to the bottom and contact with the hydrophilic surface, penetrating it, while oil is left on the surface [22–24]. This phenomenon gives

*Corresponding author. E-mail: fail_23@bk.ru

an opportunity for separation of oil/water mixtures using gravitational effect excluding any energy consumption.

The aim of this study is to fabricate a hydrophilic and oleophobic membrane using stainless steel mesh with different dimension of its openings as a substrate by coating it with a developed specific compound that determines the type of wettability of resulting membrane. Developed compound consists of polymer dispersion with SiO_2 nanoparticles. The resulting coating is hydrophilic, can be easily wetted by water, meanwhile it is strongly repellent to organic liquids. Hydrophilic and oleophobic materials are not subject to fouling as well the type of their wettability allows separate mixtures of water and oily liquids using gravitation.

2. Experimental

Poly(diallyldimethylammonium chloride) (PDDA) (M.W. 100 000 g/mol, 35% aqueous solution), pentadecafluorooctanoic acid (PFOA), SiO_2 nanoparticles (average particle size 2 μm) were purchased in Sigma Aldrich and used without further purification.

2.1. Synthesis of hydrophilic and oleophobic coating

For obtaining the hydrophilic-oleophobic composition, silicon nanoparticles (0.1 g) were dispersed in an aqueous solution of PDDA (35 ml, 1 mg/ml) by sonication for 30 min. After creating a homogeneous dispersion of silicon nanoparticles in a PDDA solution, 8 ml of 0.1 M of PFOA was added dropwise to the mixture under stirring. When a certain concentration of PFOA was reached, a precipitate was formed in the mixture due to coordination of anions of PFOA with quaternary amine groups of PDDA. The resulting precipitate was washed several times with distilled water and then dried at room temperature.

A certain amount of dried precipitate of PDDA/PFOA/SiO_2 was dissolved in ethanol and the resulting mixture was deposited on the substrate – a pre-cleaned stainless steel mesh with certain dimensions of its openings, by dip-coating method. Coated mesh was dried at room temperature for 2 h until complete evaporation of ethanol and then exposed to a 50 W microwave plasma treatment for one minute with the formation of polar hydrophilic groups on its surface in order to enhance the hydrophilicity of the membrane.

2.2. Study of hydrophilicity and oleophobicity of the resulting membranes

To determine the degree of hydrophilicity and oleophobicity of surface of obtained membrane, the wetting angle between its surface and the drop of liquid (water or organic liquid) was measured. Based on the value of measured angle, conclusions on the degree of hydrophilicity and oleophobicity of the sample were made.

2.3. Study of surface morphology of membranes by SEM

The investigations on the surface morphology of obtained samples were carried out on a microscope QUANTA 3D 200i (FEI, USA) with an accelerating voltage of 30 kV. For studies the sample was attached to a copper holder using a conductive adhesive or tape.

2.4. Study of efficiency of oil/water separation by obtained hydrophilic-oleophobic membrane

Study of the efficiency of separation of water and organic liquids using obtained hydrophilic-oleophobic membranes was carried out on a self-assembled installation that consists of two mutually screwed stubs and glass tubes attached to them. Membrane of a certain diameter was placed into the internal cavity of the stub, where it was tightly sealed at the top and bottom by rubber seals. After stubs were tightened, thereby ensuring the impermeability of the entire system to eliminate the slightest leakage.

A mixture of water and organic liquid in certain ratios was introduced into the assembled system from the top through a glass tube, after which the liquids were stratified by the densities. In the case of using organic liquids of lower density than water, water flows to the bottom and contacts with the surface of the membrane. After complete wetting of the surface of the membrane, water penetrates through the membrane due to the hydrophilicity of its surface, gravitational forces and pressure of the column of liquids. At the same time, the volume and rate of separation of water from the oil/water mixture, as well as the presence of organic liquids in separated water were investigated.

3. Results and discussion

Synthesized compound based on PDDA/PFOA and SiO_2 nanoparticles is characterized by interactions of functional groups of various wettability – fluorinated groups together with carboxyl and ammonium groups results in hydrophilic and oleophobic type of wettability of composition. A thin film of this composition was sprayed on substrate in order to study its surface morphology, SEM images of which are presented in Fig. 1.

A film based on PDDA/PFOA/SiO_2 sprayed on surface of a flat substrate is presented by a textured surface with a high roughness, a large number of surface formations and pores. As the resolution is increased, it can be seen that the surface of the coating is presented by spherical SiO_2 nanoparticles, which are fixed at the surface by polymer and arranged in a chaotic manner. The average diameter of the SiO_2 nanoparticles is approximately 3 μm (Fig. 1). It is evident that existence of SiO_2 in the structure increases the roughness of the surface formatting pores and protrusions of different sizes. It was experimentally found that increase amount of SiO_2 nanoparticles in mixture forms the surface with less smooth areas and more aggregates.

Stainless steel meshes of different dimensions of their openings (mesh 100, 200 and 400) were chosen as a substrate for obtaining of membranes due to advantages of their use: good mechanical strength, easy maintaining sizes of their opening by varying the type of used mesh and easy recycle after their use through remolding.

The uniformity of coating mesh with different dimensions of their openings using SEM have been studied, since the uniformity of coating plays an important role in achieving the desired wettability of membrane.

Figure 2 presents the study of surface morphology of non-coated and coated meshes with different dimensions of openings (100, 200 and 400) by mixture of PDDA/PFOA and SiO_2 nanoparticles. Coating of meshes was conducted by dip-coating method.

It is evident from Fig. 2a that in case of stainless steel mesh 100 the coating is not uniform along the surface of mesh. SiO_2 nanoparticles are located on the walls of wires of mesh in chaotic manner and polymer serve as adhesion layer. After coating the diameter of wires of mesh 100 increased in average from 129 up to 144 μm.

Figure 2b presents the quality of coating of the surface of mesh 200 by PDDA/PFOA and SiO_2 nanoparticles. It is visible that the quality of coating of mesh 200 along the surface of wire is more uniform comparing to the coating of mesh 100. Coating is presented by thinner film, since the diameter of coated wires has increased in average by 7 μm.

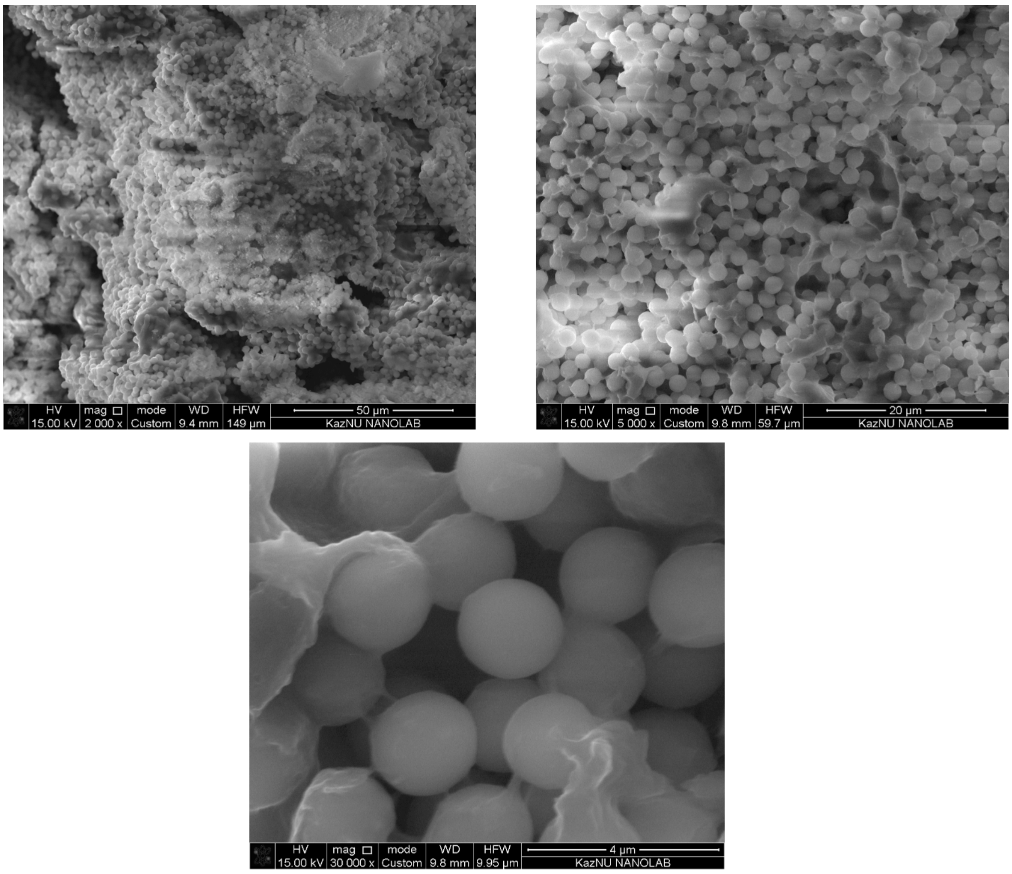

Fig. 1. SEM of film based on PDDA/PFOA and SiO_2 nanoparticles.

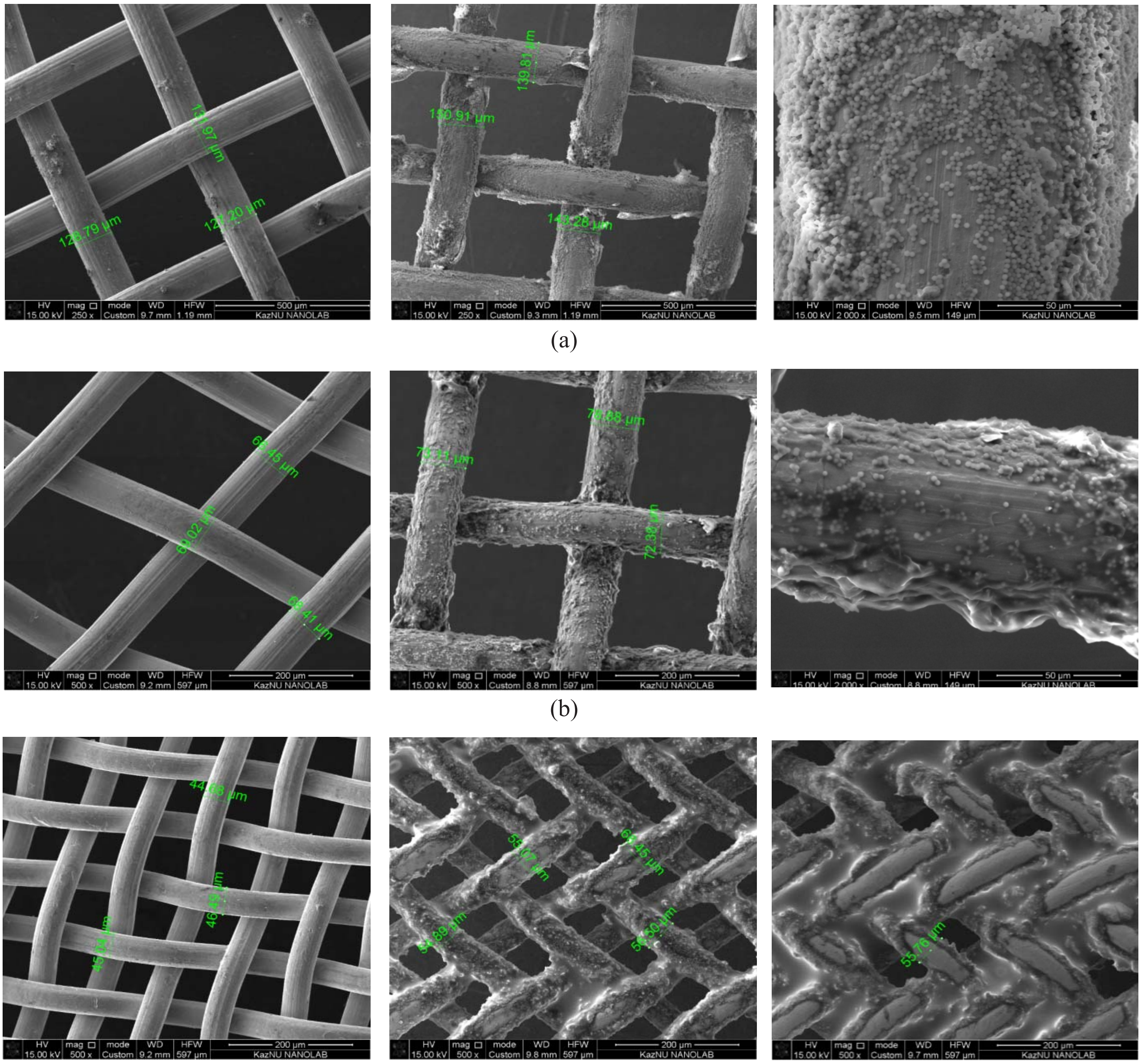

Fig. 2. Study of quality of coating of meshes 100 (a), 200 (b) and 400 (c) by PDDA/PFOA and SiO_2 nanoparticles.

From Fig. 2c it is visible that the coating of mesh 400 is uniform along the whole surface of wires of mesh. The coating based on PDDA/PFOA and SiO_2 is rough with lots of surface agglomerates. The diameter of wire has increased in average by 10 µm. Due to smaller dimensions of openings of mesh 400, some clogging of pores are occurred which in turn may impact on separation efficiency of membrane.

Study of degree of oleophobicity and hydrophilicity of obtained membranes was carried out by measuring the wetting angle between surface of membranes and a drop of tested liquid (water and organic liquid). It was found that membrane based on mesh 100, coated with PDDA/PFOA and SiO_2 nanoparticles does not demonstrate oleophobicity of its surface. Both, a drop or organic liquid (kerosene) and a drop of water easily penetrate the structure of membrane.

Membranes based on stainless steel meshes 200 and 400 coated with PDDA/PFOA and SiO_2 nanoparticles demonstrate hydrophilic and oleophobic properties. In case of membrane based on mesh 200 the wetting angle of its surface and a drop of dyed kerosene is 103°, while the drop of water penetrates structure of membrane easily. Wetting angle is increased up to 116° in case of membrane based on mesh 400 coated with PDDA/PFOA and SiO_2 nanoparticles (Fig. 3).

Table

Investigation of the efficiency of separation of organic liquids and water by synthesized membranes

Type of membrane	Time for the passage of liquid through the membrane		
	Water, 20 ml	Vacuum pump oil, 10 ml	Kerosene, 10 ml
Stainless steel mesh 100 coated with PDDA/PFOA/SiO_2	4–5 sec	18–19 sec	7–8 sec
Stainless steel mesh 200 coated with PDDA/PFOA/SiO_2	4–5 sec	10–12 min	14–15 min
Stainless steel mesh 400 coated with PDDA/PFOA/SiO_2	4–5 sec	20–21 min	does not pass

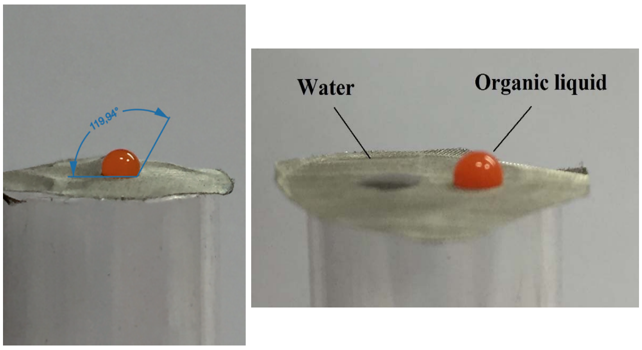

Fig. 3. Wetting angle of membrane based on stainless steel mesh 400 coated with PDDA/PFOA and SiO_2 nanoparticles.

Taking into account results of the values of the wetting angles of synthesized membranes, further investigation of the efficiency of separation of water and organic liquids were carried out only for membranes based on stainless steel meshes 200 and 400, since membranes based on mesh 100 did not demonstrate oleophobic properties.

Figure 4 shows the process of separation of mixture of water and dyed kerosene by obtained hydrophilic-oleophobic membrane based on stainless steel mesh 400 coated with a polymer of PDDA/PFOA/SiO_2. It can be seen that membrane effectively passes water (20 ml of water in 4–5 sec), but after the complete penetration of water through structure of this membrane, dyed kerosene does not penetrate through its structure due to its strong oleophobicity. Resulting hydrophilic-oleophobic properties of obtained membrane are caused by fluorinated constituents, which are remained in mobile state at the surface. When water contacts with surface of coated membranes, fluorinated groups may be reorganized to allow water penetration through hydrophilic surface [25–28].

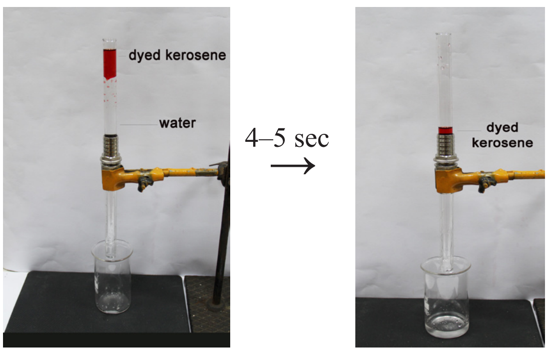

Fig. 4. Study of the efficiency of oil/water separation using hydrophilic and oleophobic membranes.

Table presents the average values of rate of penetration of various types of liquids through membranes based on stainless steel meshes (100, 200 and 400), coated with PDDA/PFOA/SiO_2. It can be seen from the Table that in case of the mesh 100, water, vacuum pump oil and kerosene penetrate this membrane with a relatively high rate. This phenomenon depends on large size of the openings of the mesh 100, due to which its coating does not change the wettability of the mesh.

In case of a membrane based on the mesh 200 coated with PDDA/PFOA/SiO_2, the rate of penetration of 20 ml of water is rather high – 4–5 sec, while the time of penetration of 10 ml of vacuum pump oil and kerosene through membrane is decreased to 10–12 and 14–15 min, respectively. When comparing these results with the results of the rate of penetration of liquids through the mesh 100, it can be assumed that the mesh 200 coated with PDDA/PFOA/SiO_2 exhibits hydrophilic-oleophobic properties, but this is not sufficient for their possible use in separation of water and organic liquids. In its turn, mesh 400 coated with PDDA/PFOA/SiO_2 exhibits excellent hydrophilic properties, the rate of penetration of 20 ml of water is 4–5 sec (as in the case of a mesh 200), and however, this membrane does not allow kerosene to penetrate through its structure. Even after contacting of column of 10 ml of kerosene with the surface of membrane, no penetration of kerosene through membrane was observed. The rate of penetration of 10 ml of vacuum pump oil decreased to 20–21 min.

4. Conclusions

A simple and inexpensive approach in formation of hydrophilic and oleophobic membranes was shown in this paper. A rough structure of membranes based on stainless steel meshes 200 and

400, coated with PDDA/PFOA/SiO_2 demonstrate simultaneous hydrophilic and oleophobic properties. It was found that membrane based on stainless steel mesh 400 coated with PDDA/PFOA/SiO_2 possess strong oleophobicity to kerosene, while 20 ml of water penetrates it during 4–5 sec. Obtained membranes are excellent candidates for selectively separation of mixtures of water and organic liquids by simple gravitational separation with important advantages of anti-fouling and easy recycling comparing to traditional oil/water separation materials.

Acknowledgement

Scientific results was conducted in the framework of project #AP05131745 "Obtaining of micro and nanoporous membranes of special type of wettability for complex purification of water from organic pollutants and salts" with support of Ministry Education and Science of Republic of Kazakhstan.

References

[1]. L. Jiang, Z. Tang, R.M. Clinton, D.W. Hess, V. Breedveld, *Cellulose* 23 (2016) 3885–3899. DOI: 10.1007/s10570-016-1048-1
[2]. L. Feng, Z.Y. Zhang, Z.H. Mai, Y.M. Ma, B.Q. Liu, L. Jiang, D.B. Zhu, *Angew. Chem. Int. Ed.* 43 (2004) 2012–2014. DOI: 10.1002/anie.200353381
[3]. T.T. Lim, X.F. Huang, *Chemosphere* 66 (2007) 955–963. DOI: 10.1016/j.chemosphere.2006.05.062
[4]. Y.Z. Cao, X.Y. Zhang, L. Tao, K. Li, Z.X. Xue, L. Feng, Y. Wei, *ACS Appl. Mater. Interf.* 5 (2013) 4438–4442. DOI: 10.1021/am4008598
[5]. L. Feng, Z. Zhang, Z. Mai, Y. Ma, B. Liu, L. Jiang and D. Zhu, *Angew. Chem. Int. Ed.* 116 (2004) 2046–2048. DOI: 10.1002/ange.200353381
[6]. X. Huang, T.T. Lim, *Desalination* 190 (2006) 295–307. DOI: 10.1002/ange.200353381
[7]. F.R. Sultanov, B. Bakbolat, Z.A. Mansurov, Rabi Ebrahim, Ch. Daulbayev, A.A. Urazgalieva, M.I. Tulepov, *Euras. Chem. Tech. J.* 19 (2) (2017) 127–132. DOI: 10.18321/ectj286
[8]. F. Sultanov, B. Bakbolat, Ch. Daulbaev, A. Urazgalieva, Z. Azizov, Z. Mansurov, M. Tulepov, S.S. Pei, *J. Eng. Phys. Thermophys.* 90 (2017) 826–830. DOI: 10.1007/s10891-017-1631-9
[9]. H. Hu, Z.B. Zhao, W.B. Wan, Y. Gogotsi, J.S. Qiu, *Adv. Mater.* 25 (2013) 2219–2223. DOI: 10.1002/adma.201204530
[10]. G.T. Smagulova, S. Kim, N.G. Prikhod'ko, B.T. Lesbayev, A.V. Mironenko, A.A. Zakhidov, Z.A. Mansurov, *Int. J Self-Propag. High-Temp. Synth.* 25 (2016) 173–176. DOI: 10.3103/S1061386216030122
[11]. Z. Xue, S. Wang, L. Lin, L. Chen, M. Liu, L. Feng, L. Jiang, *Adv. Mater.* 23 (2011) 4270–4273. DOI: 10.1002/adma.201102616
[12]. R.C.B. Lemons, E.B. de Silva, A. dos Santos, R.C.L. Guimaraes, B.M.S. Ferreira, R.A. Guarnieri, C. Dariva, E. Franceschi, A.F. Santos and M. Fortung, *Energy Fuels* 24 (2010) 4439–4444. DOI: 10.1021/ef100425v
[13]. W.B. Zhang, Y.Z. Zhu, X. Liu, D. Wang, J.Y. Li, L. Jiang, J. Jin, *Angew. Chem. Int. Ed.* 53 (2014) 856–860. DOI: 10.1002/anie.201308183
[14]. M.H. Tai, J. Juay, D.D. Sun, J.O. Leckie, *Sep. Purif. Technol.* 156 (2015) 952–960. DOI: 10.1016/j.seppur.2015.08.008
[15]. P. Patel, C.K. Choi, D.D. Meng, *JALA* 15 (2010) 114–119. DOI: 10.1016/j.jala.2009.10.012
[16]. S.J. Pastine, D. Okawa, B. Kessler, M. Rolandi, M. Llorente, A. Zettl, J.M.J. Frechet, *J. Am. Chem. Soc.* 130 (2008) 4238–4239. DOI: 10.1021/ja8003446
[17]. J.K. Yuan, X.G. Liu, O. Akbulut, J.Q. Hu, S.L. Suib, J. Kong, F. Stellacci, *Nat. Nanotechnol.* 3 (2008) 332–336. DOI: 10.1038/nnano.2008.136
[18]. N.R. Chiou, C. Lu, J. Guan, L.J. Lee, A.J. Epstein, *Nat. Nanotechnol.* 2 (2007) 354–357. DOI: 10.1038/nnano.2007.147
[19]. M. Jin, J. Wang, X. Yao, M. Liao, Y. Zhao, L. Jiang, *Adv. Mater.* 23 (2011) 2861–2864. DOI: 10.1002/adma.201101048
[20]. D. Zahner, J. Abagat, F. Svec, J.M.J. Frechet, P.A. Levkin, *Adv. Mater.* 23 (2011) 3030–3034. DOI: 10.1002/adma.201101203
[21]. L. Chen, M. Liu, H. Bai, P. Chen, F. Xia, D. Han, L. Jiang, *J. Am. Chem. Soc.*131 (2009) 10467–10472. DOI: 10.1021/ja9019935
[22]. P.S. Brown, O. Atkinson, J.P.S. Badyal, *ACS Appl. Mater. Interf.* 6 (2014) 7504–7511. DOI: 10.1021/am500882y
[23]. J. Yang, L.T. Yin, H. Tang, H.J. Song, X.N. Gao, K. Liang, C.S. Li, *Chem. Eng. J.* 268 (2015) 245–250. DOI: 10.1016/j.cej.2015.01.073
[24]. X.Y. Zhu, W.T. Tu, K.H. Wee, R.B. Bai, *J. Membr. Sci.* 466 (2014) 36–44. DOI: 10.1016/j.memsci.2014.04.038
[25]. R.A. Lampitt, J.M. Crowther, J.P.S. Badyal, *J. Phys. Chem. B.* 104 (2000) 10329–10331. DOI: 10.1021/jp002234a
[26]. H. Sawada, H. Yoshioka, T. Kawase, H. Takahashi, A. Abe, R. Ohashi, *J. Appl. Polym. Sci.* 98 (2005) 169–177. DOI: 10.1002/app.22034
[27]. J.A. Howarter, J.P. Youngblood, *Adv. Mater.* 19 (2009) 3838–3843. DOI: 10.1002/adma.200700156
[28]. S. Turri, R. Valsecchi, M. Vigano, M. Levi, *Polym. Bull.* 63 (2009) 235–243. DOI: 10.1007/s00289-009-0083-6