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Synthesis and characterization of semi-permeable graphene/graphene oxide membranes for water desalination

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ABSTRACT

In this paper, we present novel semi-permeable graphene-based membranes. Composite filters were designed and fabricated on polysulfone porous scaffolding using combinations of polycrystalline large-area High Strength Metallurgical Graphene (HSMG®), graphene oxide, hydrazine and an in-situ interfacial polymerized polyamide. The naturally occurring defects in HSMG® (which were tenths of a nanometer) were the clue in fabricating a filtering membrane. The performance of graphene membranes was evaluated in forward osmosis test. The prepared composites were proved to be semi-permeable membranes with great ions blocking efficiency (over 95%) and water flux only one order of magnitude lower than the commercial reverse osmosis membranes. The experiments' results demonstrated that the solutions proposed in this work indicate that graphene-based membranes can be used in water treatment technology.

Introduction

Life of most living organisms on Earth is dependent on access to clean water. Over one billion people live in areas which suffer from water shortages [1]. For this reason, in order to ensure the right quality of potable water, various technical solutions as well as physicochemical phenomena are used to reduce the concentration of various types of impurities. The removal of ions and particles can be carried out by filtration, using reverse osmosis process, by ion exchange resins or electrodeionization, for example. Membrane processes deserve special attention as they are widely used in water treatment [2]. Membrane technologies—due to their low cost, easy maintenance and high rejection rate—have gained popularity during the last few decades and are widely used in very specific applications [3, 4].

Progress in discovering new materials and developing new nanotechnologies meant that intense

research carried out is aimed at replacing composites which are currently used and are based on polymers in membrane technology by new-generation nanomaterials such as graphene, carbon nanotubes (CNTs), graphene oxide (GO) and other 2D materials [2, 5–8]. Carbon-based nanomaterials are particularly interesting because of their unique properties, such as large surface area, large porosity range and exceptional mechanical strength. Smooth friction-free graphite walls of carbon nanotubes and graphene, as well as a fast sorption–desorption mechanism, can facilitate the transport of water molecules, ensuring high efficiency of flux separation. Unfortunately, the high-cost sourcing and difficulties in fabricating of 3D well-aligned carbon nanotube arrays-based membranes make their wide commercial use very difficult.

An important issue in membrane processes is gaining a high level of permeability per unit of pressure while providing a high rejection rate as well as resistance to oxidation and fouling [2].

The solutions proposed currently, based on 2D materials, allow working near a thermodynamic limit with a pressure which is only 10–20% higher than osmotic pressure [5].

Desalination using nanoporous graphene membranes and composites with graphene oxide is realized by the exclusion of ions by filtration, which is connected with the size of pores, the distance between the graphene sheets or electrostatic interactions. The distance should fall within a range of 0.3–0.7 nm to make water flow possible (the water molecule diameter of 0.27 nm [8]) while separating pollution ions. Defect-free graphene sheet, according to information from the literature, is an ideal barrier for gases and liquids [6]. Moreover, this material has exceptional chemical [9] as well as mechanical properties [10] and is the thinnest possible layer with a thickness of only 1 atom. That is why defects purposely made in graphene with the use of plasma, laser beam perforation and selective oxidation [11], electron beam [12], ionic etching [13, 14] and ion bombardment [15] give the possibility to make a layer which is nanoporous and can be used as a membrane.

Polycrystalline graphene synthesized on the liquid copper (HSMG®—High Strength Metallurgical Graphene) has special properties as defects with a size of a tenth of a nanometer can be found in its structure [16, 17]. Aside from the desired size defects, the large-area HSMG® graphene sheets also contain large

defects resulting from synthesis and/or transfer onto another substrate, which make effective separation impossible.

Among the methods of sealing these defects, it is worth mentioning the interfacial polymerization of nylon from two precursors separated by the membrane [7], the deposition of metals and the metal oxide which uses atomic layer deposition (ALD) in discontinuities on defects borders [8].

In several studies on composite graphene membranes, we also met membranes based on graphene oxide or graphene powder, manufactured from liquid suspension and strengthened with binder [18] as well as layers of graphene, graphene oxide or their combination applied on polymeric nanofiber surface [19]. The method of laying graphene oxide on the surface has a huge impact on the positioning and orientation of material flaxes. Gravitational coating of load-bearing oxide causes chaotic distribution in the layer created and large uncontrolled porosity [20]. A high GO orientation degree is gained using a pressure-assisted method or spin coating [21]. Due to the water pressure applied, membranes have to be manufactured on scaffoldings, e.g., metallic, ceramic or polymeric ones, depending on the application in forward osmosis or reverse osmosis [22].

In our study, graphene oxide was used as an effective sealing matter, which can form a thin and strong layer, especially when its flakes were subjected to nanostructurization.

In the presented work, centimeter-scale membranes with a large-area polycrystalline HSMG® graphene transferred onto polysulfone (PSU) commercial microfiltration membranes were prepared. We utilized novel composite membranes' advantages which result from graphene synthesis on liquid copper. Detected subnanometric defects are a clue for the use of HSMG® graphene in filtration technology. However, due to the large defects in graphene generated during transfer on porous substrates, such membranes are not effective. These defects must be eliminated. For this purpose, graphene oxide, hydrazine and/or nylon were applied. Graphene oxide in various types of configuration—with additional nanostructurization with hydrazine and/or nylon interfacial polymerization sealing—was prepared to obtain the best water permeance and ion rejection rate. Membranes under the influence of an osmotic pressure gradient caused by a NaCl concentration difference revealed their semi-permeable

properties, such as ion transport blocking while allowing water flux to go through the membrane. This shows that prepared composites have the potential to be used in water treatment technology.

Experimental

Characterization of materials

Graphene HSMG®

Graphene for building the composite was obtained using the metallurgical method. Graphene HSMG® synthesis and substrate preparation were carried out according to the procedure which was made a patent (Method of producing graphene from liquid metal, US 9 284 640, USA) [16, 17, 23]. The substrate for crystallization of graphene was a Cu–Ni sheet. A nickel foil with a thickness of 0.15 mm was coated with electroplated copper in a saturated solution of copper sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$). The current density was 2 A dm^{-2}, the processing time lasted 6 hrs, and the obtained thickness equalled 0.2 mm. Monolayer sheets of HSMG® graphene were produced in a vacuum furnace.

The following process parameters were applied:

- heating in a vacuum (pressure 10 Pa) to a temperature of 1060 °C,
- carburizing of the Cu–Ni substrate in an ethylene–acetylene–hydrogen gas mixture (four alternating stages of gas dosing and isothermal annealing, during which the carburizing atmosphere was dosed during 5 s, followed by annealing in a vacuum for 600 s) at a temperature of 1060 °C,
- heating in an argon and hydrogen gas mixture to a temperature of 1100 °C under 2 kPa pressure
- isothermal annealing at a temperature of 1100 °C for 5 min,
- cooling in an argon and hydrogen atmosphere to an ambient temperature.

The graphene produced was subjected to qualitative tests by optical microscopy on a Cu–Ni substrate. The surface was washed with water before analysis. The exposure time was about 2 min. Copper may be oxidized this way in places not covered with graphene, thus revealing macroscopic discontinuities in the graphene layer. The purpose of this operation was to select substrates with graphene for further

proceedings in the planned tests, i.e., without signs of any change in copper color. Randomly selected places, after treatment with 0.1 M $FeCl_3$ solution (exposure time was 5 s), were analyzed using a microscope (Fig. 1).

$FeCl_3$, as a strong oxidant, reacts very quickly with copper, hence why it is used to remove copper substrates after graphene synthesis. $FeCl_3$ gets under the graphene layer, where it penetrates and digests the metal. Dark spots which appear in the microscopic image (Fig. 1) reflect discontinuities in the layer—definitely extended by the residual metal etching products.

Next, Raman spectroscopy was used for the investigation. The measurements were made using a laser wavelength of 532 nm; the laser power
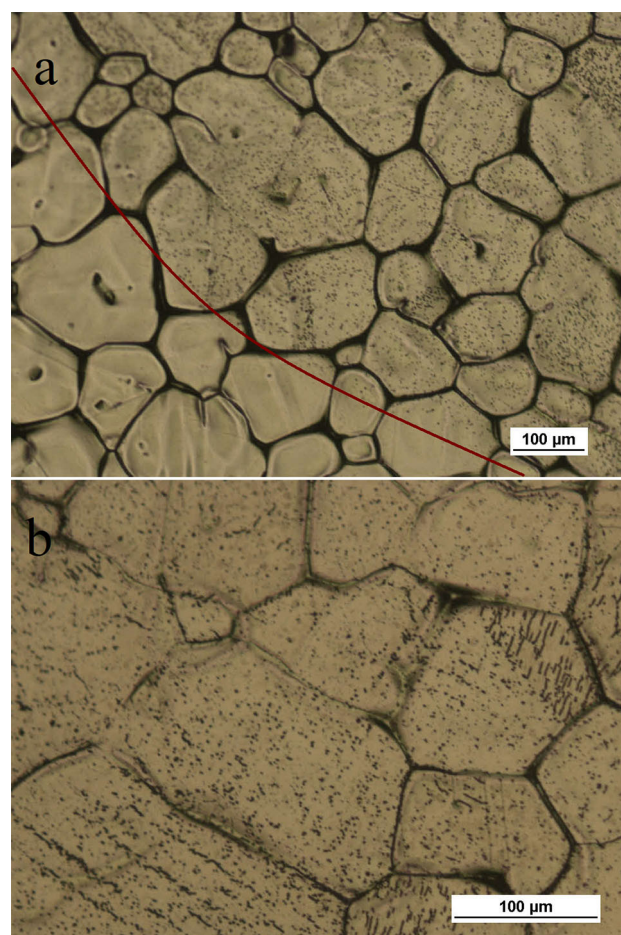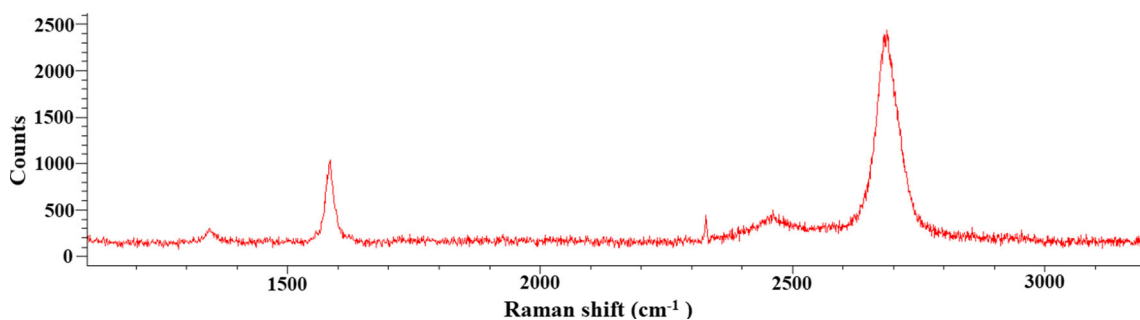

Figure 1 Cu–Ni substrate surface with a graphene layer—results of the treatment with 0.1 M $FeCl_3$ solution. Optical microscope image at different magnifications. **a** Visible boundary of the $FeCl_3$ operating field and intact area of the copper matrix (a border marked with the red line); **b** the place after act of $FeCl_3$ under higher magnification.

delivered to the sample was 10 mW. When analyzing the Raman spectra of the graphene, attention was paid to the presence and the intensity of graphene-specific peaks (G 1580 cm^{-1} and 2D 2690 cm^{-1}) as well as to the peaks indicative of the scale of defects within the graphene structure (D 1350 cm^{-1} and D′ 1620 cm^{-1}). The Raman spectra obtained showed the presence of a graphene monolayer on the growth substrate (Fig. 2). A TEM examination was used to assess the nanostructure of the graphene layers produced. A TEM Talos F200X from FEI was used in the research. This is an atomic resolution microscope with a maximum voltage which accelerates electrons of 200 kV. Based on these studies, nanostructural defects of a size from 0.2 to 0.5 nm were identified (Fig. 3).
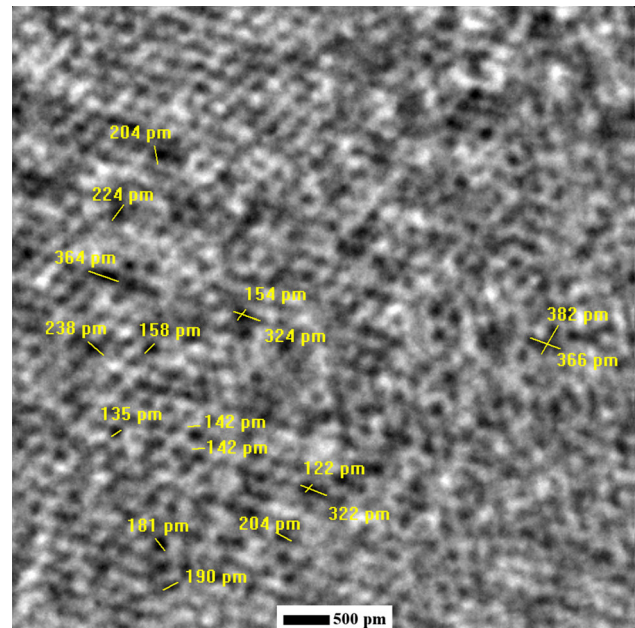
Polysulfone membrane

MicroPES® 1F EL porous support substrate—made by *Membrane GmbH*, Germany—was used to prepare composite graphene membranes. Membrane thickness equals 110 μm with an average pore size of 0.2 μm and water permeability at a temperature of 25 °C of ≥ 10 ml min^{-1} cm^{-2} bar^{-1}. The membranes were characterized by varying porosity in the cross section.

Figure 4a shows one side of this membrane—the major porosity side. The pore diameter on this side of the membrane is from 0.2 to 1.5 μm. The density of the pores is 0.26×10^6 mm^{-2}. Figure 4b shows the side of a polysulfone membrane with minor porosity. The pore diameter on this side of the membrane is from 0.1 to 1.0 μm. The density of the pores is 1.05×10^6 mm^{-2}. We always transferred graphene to the surface with minor porosity. Exactly the same type of polysulfone membranes was used in each test.


Figure 3 Point defects of the graphene HSMG® atomic structure. HRTEM image.

GO and rGO platelets

Graphene oxide with 0.1% dispersion in water (1 mg/1 ml) was purchased from the *Advanced Graphene Products Company*, Poland. FTIR analysis confirmed the purity and oxidation state of the material used in our studies and provided an excellent reference to the result obtained by GO flakes hydrazine treatment on the polysulfone membrane (Fig. 5c).

20 μl of a 1% aqueous hydrazine solution was used per 1 cm^2 of the membrane surface. The hydrazine solution was pipetted gently on top of the composite membrane and left to react with graphene oxide for at least 120 min. The membrane was then rinsed several times by immersion in a water bath and was then air-dried.

Figure 2 Raman spectrum of graphene.
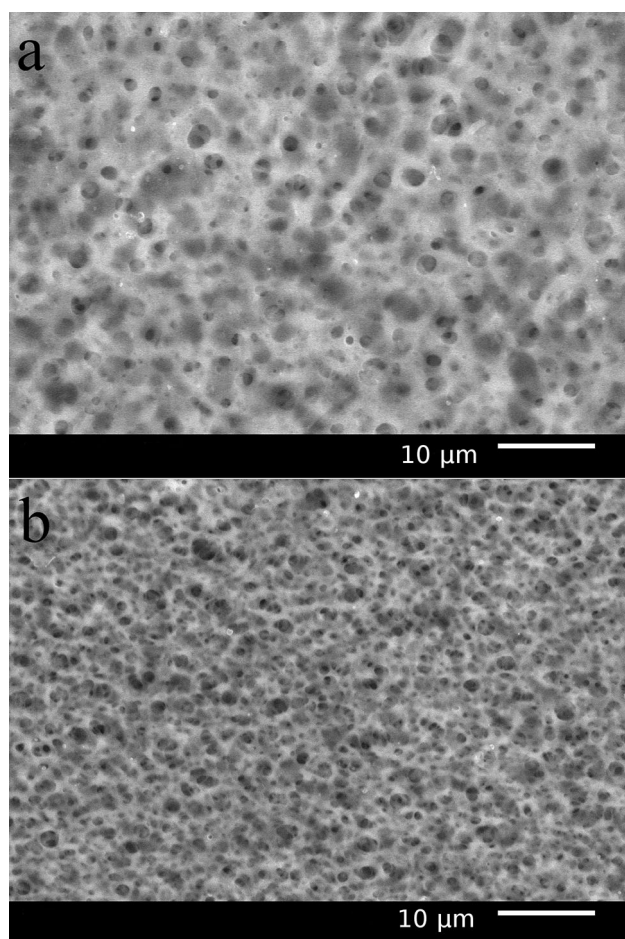
Figure 4 The polysulfone membrane structure. **a** The major porosity side, **b** the minor porosity side. SEM SE image, LSEI mode, 20 kV.

The 1% hydrazine solution was prepared by diluting commercial 80% hydrazine hydrate from *POCh*, Poland, immediately before use.

Solvents and reagents

Monomers used in the synthesis of polyamide in graphene defects on the surface of composite membranes were 98% 1,6-diaminohexane (*Alfa Aesar*, *Thermo Fisher Scientific*, Great Britain) and 92% sebacoyl chloride (*Sigma-Aldrich*). Cyclohexane (*Chempur*, Poland) was a solvent of sebacoyl chloride.

Poly(methyl methacrylate) (PMMA) with a molecular weight of 996000 g/mol of the *Aldrich Chemistry Company*, dissolved in chlorobenzene (*Chempur*, Poland) with a concentration of 0.05 mol dm^{-3} (4.6 g of PMMA—100 ml of chlorobenzene), was applied to

coating the graphene substrate in the transfer procedure.

The solvent used to dissolve and remove the PMMA foil (graphene support during the transfer on the polysulfone membrane) was 2-propanol with a technical grade of 70% (*Chempur*, Poland).

Sodium chloride was used in the osmotic transport experiments (*Chempur*, Poland). The starting concentration of NaCl in the water was c = 0.2 mol dm^{-3}.

Construction and characterization of semi-permeable composite membranes

The HSMG® graphene layer is the basic and active element of composite filtration membranes. Separation of the HSMG® graphene from the growth matrix, its transfer to the target substrate—depending on the role of this matter—and the purpose of using the constructed composite are necessary to take advantage of the extraordinary properties of graphene. In the case of designed filters, the polysulfone membrane is a carrier substrate for the HSMG® graphene. The most convenient method of the graphene transfer on the scaffolding is therefore using the PMMA transfer method.

Having formed a thin PMMA film directly on the growth matrix of graphene, the graphene layer was separated from the metallic substrate by electrochemical delamination [24]. High efficiency of that process is its main advantage. There is no risk of adsorbing of undesirable chemical etching products on the graphene surface and in the graphene defects [25]. Moreover, this method allows to use repeatedly the Cu/Ni matrix in the growth of HSMG® graphene as well as in the delamination cycles. In the case of graphene transfer to the polysulfone membrane, the polymeric support was removed in isopropanol vapors because the polysulfone could be damaged by acetone, which is typically used to dissolve PMMA.

The multiple transfer was applied by overlapping three layers of graphene in order to eliminate defects in the graphene layer arising during the transfer as well as those resulting from the specifics of the synthesis of the graphene on the liquid substrate. Another solution was to cover any defects with graphene oxide flakes with the option of cross-linking with hydrazine [26]. The next concept was using polyamide synthesis in discontinuities of the composite filtration membrane built on the basis of graphene and graphene oxide.

Figure 5 SEM, AEE mode images of: **a**—a graphene (GR) on PSU, chosen purposely with large defects to show better the mechanism of sealing; **b**—a graphene on PSU with graphene oxide (GO) coating; c – a graphene on PSU with GO coating, nanostructurized with hydrazine; Scale bar 200 μm.
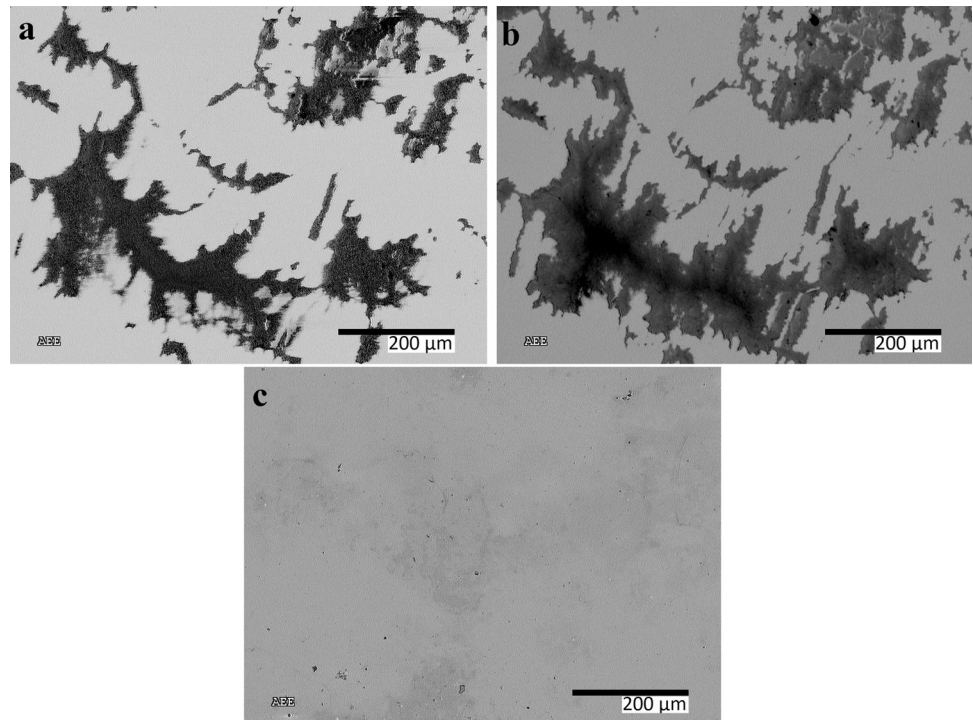
Graphene transfer on Polysulfone

Graphene samples with a size of 30 × 30 [mm^2] were prepared. Coating with PMMA in chlorobenzene as a temporary carrier layer was performed by means of drop/blade coating. The polymer dried for 30 min at a temperature of c.a. 40 °C formed a thin flexible film. Delamination of the graphene on the polymeric support was carried out using a homemade half-automatic laboratory station in 0.5 mol/l NaOH solution at a constant voltage 4.5 V at a sample submersion angle of 35° and a submersion linear speed of 0.02 mm s^{-1}. The polymer foil with graphene was placed on wetted polysulfone membrane, pressed and annealed on a heating plate at 70 °C for 5 min. The composite, formed in such a way, was then put into a chamber with boiling isopropanol to remove the PMMA layer supporting graphene.

Sealing of defects in the graphene layer

Graphene oxide (GO) as sealing species

The graphene layer on the polysulfone membrane was covered with graphene oxide flakes that were suspended in a water–isopropanol system (2:1, v/v)

at a concentration of $c = 0.0067$ g/ml and in the amount of 20 μl per 1 cm^2 of the graphene surface. Each time before use, the GO suspension in the above-mentioned solvents was dispersed by means of ultrasound. The addition of isopropanol reduced the surface tension of commercially available aqueous GO suspensions, which facilitated the even distribution of GO on the hydrophobic graphene layer. Due to their hydrophilic nature, the graphene oxide flakes tended to accumulate in uncovered places of the polysulfone during evaporation of the liquids from the membrane surface.

The SEM analysis of this surface (Fig. 6) revealed that graphene oxide effectively aggregated in discontinuities of the HSMG® layer to form a more or less dense structure.

A thin coating of GO flakes was clearly visible on the surface of the polysulfone membrane uncovered with the layer of HSMG® graphene (lighter area in Fig. 6). On the continuous graphene layer, only fragments of aggregated GO flakes could be found.

The method of applying GO flakes to cover the membrane was modified to increase the efficiency of filling defects in the graphene layer. The membrane covered with the sealing mixture was exposed to a pressure of 3.5 bar for 1 min.
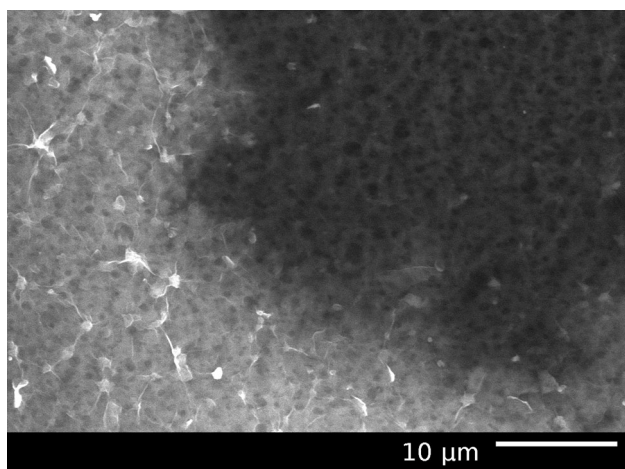
Figure 6 Polysulfone membrane coated with HSMG® graphene and filled with GO flakes. SEM image, LSEI mode, 10 kV.

Sealing composition: graphene oxide with hydrazine

The structures of the GO aggregates were strengthened by cross-linking them with hydrazine to minimize the risk of the sealing degrading during water flow. At first, a layer of GO flakes accumulated in the discontinuities of the graphene layer was treated with a 1% aqueous solution of hydrazine. In the second case, these defects were covered with a pre-cross-linked GO flakes suspension, i.e., a previously prepared mixture of GO and N_2H_4. A change in the color, from brown to black, was observed in the graphene oxide. This effect resulted from reducing the number of oxygen groups in the GO flakes and reconstructing the aromatic system in the structure of the bonds between carbon atoms (change of hybridization from sp3 to sp2 and the possibility of electronic transitions). This process led to a change in the electrical properties of the sealing layer from a non-conductive (GO) to a conductive (rGO—reduced graphene oxide) one.

The continuity of the graphene layers on the non-conductive support substrate can be examined by means of the signal of electrons absorbed by the sample (AEE mode SEM). The contrast generated during the measurement is due to the differences in currents flowing through the sample depending on whether the electron beam fell within a conductive or a non-conductive area. Dark areas against a light (i.e., conductive) background indicate the structural discontinuities within the graphene layer on the polysulfone substrate (Fig. 5a, b).

Sealing composition: graphene oxide (or graphene oxide with hydrazine) and nylon

Nylon was synthesized directly on the polysulfone membrane previously covered with the HSMG® graphene layer after sealing with GO flakes with/without hydrazine. The nylon can be prepared using interfacial polymerization. The polyamide was synthesized according to the procedure described in the literature [8]. The polysulfone membrane was placed on an aqueous amine solution (with a concentration of $c = 0.02$ g/mol) in such a way that the side covered with graphene species was in direct contact with the liquid. The other side of the membrane was gently coated with sebacoyl chloride in cyclohexane ($c = 0.01$ g/mol). The reaction was completed in 10 min. Afterward, the side in contact with amine was washed with water and the side covered by sebacoyl chloride was washed with cyclohexane. The composite obtained in such a way was air-dried at room temperature.

Filtration test and performance of composite membranes

Construction of an osmotic stand

A homemade side-by-side diffusion cell (Fig. 7) for ion separation effectiveness and water flow thought membrane examination is made of two equal chambers: one for deionized water and the other for NaCl water solution. A membrane (1) is placed in a grip (2) with a round orifice to which containers are attached (3). Each container has an inlet (4) and a graduated glass tube (5) to read the fluid volume change.
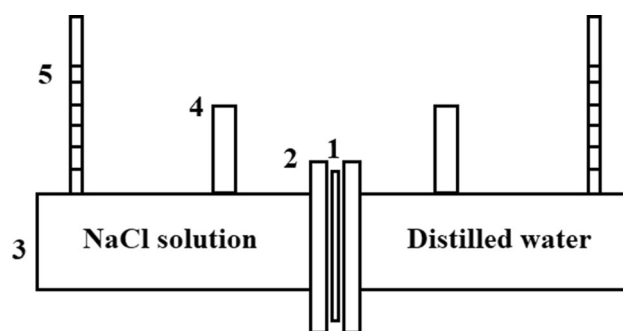
Figure 7 Scheme of a homemade side-by-side diffusion cell.

Description of the experiment

The membrane was placed in the grip and sealed up with a semiliquid polydimethylsiloxane polymer (polydimethylsiloxane (PDMS), SYLGARD^{TM} 184 Silicone Elastomer, *The Dow Corning Chemical Company*, Germany). After polymerization, the PDMS took on a solid form and stabilized the membrane. The effective membrane surface area was 4 cm^2. The membrane side with the graphene faced the chamber with NaCl water solution. The tests were conducted at a temperature of 20 °C. The osmotic pressure was 9.7 bar and was calculated on the basis of the van't Hoff equation ($\pi = vcRT$), where v is the number of ions in dissociated salt, c is the molar concentration of the solute, R is the gas constant and T is the temperature in Kelvin. Diffusion transport was studied for 24 h. The starting concentration salt in one chamber was 0.2 mol dm^{-3}, and the opposite container was filled with degassed UV lamp-treated distilled water. The measurement of water conductivity and the change in water volume on both sides of the membrane was made after each test.

The water flux through the membrane J(ml m^{-2} h^{-1} bar^{-1}) was calculated on the basis of the equation $J = \frac{V}{Atp}$, where V is the change in water volume in a container (ml), A is the membrane active surface area (m^2), t is the time (h) and p is the theoretical osmotic pressure owing to the concentration difference (bar).

Results

Different options of sealing HSMG® graphene on polysulfone membranes are listed in Table 1. The membranes' performance was evaluated during the osmotic test. Water flux was measured for each membrane composition and for the bare PSU membrane (no change in water volume in containers)

under osmotic pressure in a side-by-side osmotic cell. The ions' flux (mol m^{-2} s^{-1}) was calculated by dividing the NaCl molar concentration of the solution in a container (which contained deionized water before the test) by the test time and membrane surface. Changes in the fluid level seen on the capillary of the salt chamber allowed to estimate water flow. The results of studies on the effectiveness of blocking ions, water flux and diffusion flux of NaCl ions through composite membranes were illustrated in the form of bar charts in Figs. 8, 9 and 10, respectively.

The osmotic tests indicated that one layer of HSMG® on the PSU membrane (the A sample) was permeable to ions (blocking efficiency of 20%— Fig. 8). The opposite results were obtained for three graphene layers on the porous substrate (the B sample) as well as for the sample with pressure-assisted GO coating (the C sample), where there was neither water nor ion flux. Two graphene layers on PSU membrane with graphene oxide between them (the D sample) resulted in a rejection rate of 60% and water flux 24 ml h^{-1} m^{-2} bar^{-1}.The E sample sealed with pre-cross-linked GO flakes blocked 69% of the ions in the osmotic test. The permeance of the membrane with graphene/GO/hydrazine (the F sample) was at a level of 15 ml h^{-1} m^{-2} bar^{-1}, and a diffusion flux of 5×10^{-8} mol m^{-2} s^{-1} (Fig. 10) resulted in ion separation efficiency at a level of over 95%. The membrane with defects sealed by polyamide, either with graphene oxide or graphene oxide with hydrazine treatment (the G, H samples), resulted in an ion blocking efficiency over 90% and water permeability below 5 ml h^{-1} m^{-2} bar^{-1}.

**Table 1** Variants of membrane compositions prepared for the osmotic test

| Sample designation	Membrane composition
A	Polysulfone + HSMG®
B	Polysulfone + 3 HSMG® layers
C	Polysulfone + HSMG® + graphene oxide (pressure assisted)
D	Polysulfone + HSMG® + graphene oxide + HSMG®
E	Polysulfone + HSMG® + (graphene oxide + hydrazine solution)
F	Polysulfone + HSMG® + graphene oxide + hydrazine
G	Polysulfone + HSMG® + graphene oxide + nylon
H	Polysulfone + HSMG® + graphene oxide + hydrazine + nylon

Figure 8 Ions blocking efficiency in the osmotic test.
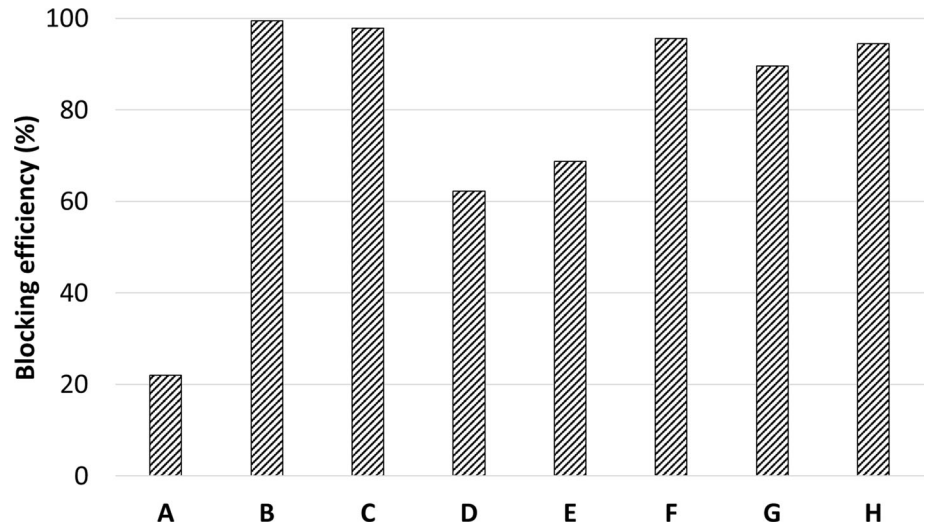
Figure 9 Results of water flux and ion flux through composite membranes.
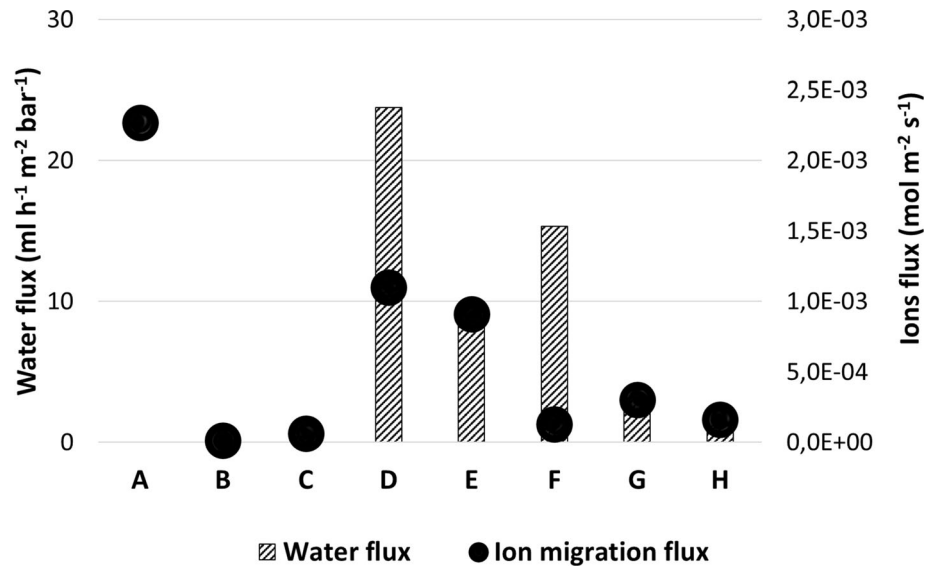
Figure 10 Diffusion flux of NaCl ions through composite membranes.
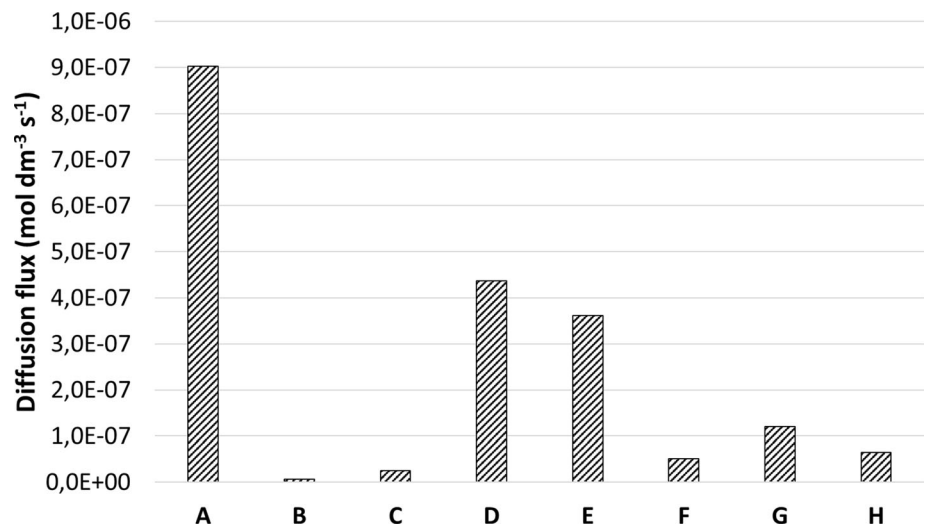
Discussion

The test showed that one layer of graphene on the PSU membrane is not enough to stop ion transport as the blocking efficiency was only 20% referring to the bare PSU membrane in a control experiment. The ions of NaCl could quite freely flow through the filter to pure water without changes in the liquid level in the capillaries. As it could be expected, this result confirmed the presence of defects larger than point defects in the atomic carbon network of the graphene layer. The transfer of larger graphene sheets involves a higher risk of deformations and disruptions in the graphene structure.

Unfortunately, the multiple transfer of graphene layers on PSU membrane did not bring the desired effect. Three overlapping layers of graphene were too hermetic and not permeable to water.

The use of graphene oxide was the other way of reduction in mechanical defects. It supplemented larger disconnections of layers to block ions in the process of salt fluid filtration, but point defects necessary for the passage of water molecules were saved. We managed to aggregate GO flakes on the PSU membrane in places uncovered with HSMG® (see Figs. 5, 6). Low stability of GO aggregates under the conditions of the experiment was the next problem to overcome. It is known that GO laminates are very susceptible to redispersal into water. Hence, graphene oxide flakes distributed on the HSMG® graphene layer could be flushed out by a flowing water stream during the filtration process. Moreover, the size of nanochannels in GO aggregates under the influence of water can significantly increase due to high hydrophilicity of GO nanosheets. These factors can negatively affect the overall selectivity of composite membranes.

In order to minimize the risk of degradation of the sealing during water flow, the GO layer was prepared from GO suspensions using the vacuum filtration method. This action was expected to forcefully penetrate the GO flakes deeper into the pores of the polysulfone membrane as well as better anchoring of the GO aggregates in graphene defects. Unfortunately, the pressure influence on the graphene oxide caused the GO flakes to be arranged so tightly that an impermeable layer was created.

The sealing made of GO flakes was covered with the HSMG® graphene layer once again. In the 'C' specimen (GO plates between graphene sheets), high water and ions flux was gained because graphene layers not bonded between GO allow the use of porosity in GO—and defects in the graphene—to transport water as well as salt ions.

The structure of GO aggregates was strengthened by cross-linking of GO flakes with hydrazine molecules which was another proposal of GO sealing protection. Mixing GO solution with hydrazine and coating it with graphene was not effective. A better solution was to first place the GO solution, let it dry and then bond the GO with hydrazine so that the GO flakes in water/alcohol solution could settle down in graphene discontinuities on the PSU surface (using the hydrophilicity of the PSU and the hydrophobicity of graphene).

Satisfactory ion blocking as well as the GO sealing protection was achieved in the case of interfacial polymerization of nylon in defects and cracks of composite membranes. Unfortunately, nylon also effectively blocked the water flux that was confirmed by the osmosis tests for F and H membranes.

In summary, the best compromise between water permeability and the rejection rate was obtained for membrane with graphene/GO/hydrazine. Water flux of 15 ml h^{-1} m^{-2} bar^{-1} is one order of magnitude lower than for commercial reverse osmosis membranes currently used [20], graphene-based membranes fabricated by O'Hern et al [8] and by M. Kafiah et al. [7]. The diffusion flux for this specimen was $5 \cdot 10^{-8}$ mol m^{-2} s^{-1}, which is two orders of magnitude lower than in experiment with NaCl presented by O'Hern et al. [8]. The diffusion flux expressed in mol dm^{-3} s^{-1} is also two orders of magnitude lower than the one presented by Kafiah et al. [7]. Most of the samples prepared in our experiment show a higher ion blocking efficiency (%) than presented in the literature [7, 27]. Adding polyamide by interfacial polymerization on our membranes helped to decrease ion flux through the membrane, but also water could not flow. The use of hydrazine reduced the oxidative area of GO flakes and decreased the possibility of forming hydrogen bonds between water molecules and hydroxyl groups. Thus, it allowed the enhancement of water transport through the tested membranes. This result was compatible with theoretical predictions regarding the water transport mechanism, which shows that oxygen groups present in GO flakes can retain the flowing water molecules near to them and increase fluid–boundary friction [28].

Conclusions

New membranes containing combinations of large-area HSMG® graphene, graphene oxide, hydrazine and polyamide on porous polysulfone scaffold were fabricated. The tenths of a nanometer size defects naturally occurring in HSMG® graphene were the basis for the design and implementation of the composite filters. GO flakes, hydrazine treatment and synthesis of interphase polymers were used to cover large discontinuities resulting mainly from the transfer process. Different sealing compositions led to different results. The composite membranes were characterized by either better ion blocking properties or revealed a greater water content under the impact of the set osmotic pressure gradient.

The optimal solution was to use a variant of sealing large HSMG® graphene defects with GO flakes treated with hydrazine. Hydrazine cross-linked and reduced the number of oxygen groups, which resulted in the improvement in the filtering properties of the entire membrane surface.

The presented composites appeared to be semi-permeable membranes with excellent effectiveness in ion transport blocking. It was two orders of magnitude better than presented in the scientific literature. At the same time, both high water flux nearing one of commercial RO membranes and graphene membranes in the scientific literature were possible. The graphene-based filters proposed in this article have proven to be useful as semi-permeable membranes in water treatment.

Acknowledgements

Compliance with ethical standards

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