Features of pulsed photon annealing of graphene oxide membranes for water desalination

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Abstract

Fabrication of reduced graphene oxide/polyvinylidene fluoride (rGO/PVDF) membranes by coating the surface of standard polymeric PVDF membranes with thin graphene oxide (GO) film is demonstrated. rGO/PVDF membranes have a better filtration efficiency than standard polymer PVDF membranes. For stabilization of rGO/PVDF membranes, a pulsed photon annealing has been used. Increase of water flow through the rGO/PVDF membranes with the decrease of the nanochannel sizes has experimentally been shown. Water transportation via planar nanochannels of rGO membranes depends on an rGO reduction time, which is explained by a decrease of the water shear viscosity activation energy in nanochannels.

1. Introduction

rGO membranes with nanoscale interlayer channels and pores are promising materials for industrial water desalination and purification due to their cost-effective fabrication technology and the rich natural reserves of graphite [1]. The most attractive feature of rGO membranes is a unique mechanism of transport of water molecules through nanoscale pores [1–4].

However, the instability of rGO membranes [1, 2, 4] limits their industrial application [5, 6]. The preparation of rGO membranes is a complex task, since they tend to agglomerate, aggregate, and collapse due to the reduced number of oxygen-containing functional groups and lower dispersibility and wettability compared to GO membranes [1]. The mechanisms of water desalination and filtration through rGO membranes are also unclear [2, 4, 5, 7].

The current GO and rGO membranes for water purification are promising for practical use due to their excellent filtering selectivity [1, 2, 4, 5, 7, 8] and a low cost with a relative simplicity of production on a large scale [1, 4, 6]. Nanochannels of GO and rGO membranes with the interlayer sizes of 0.30 nm and (0.34–0.37) nm are formed between two-dimensional GO or rGO nanosheets and are permeable for gases and ions having sizes smaller than those of the nanochannels, while blocking all other large particles.

GO membranes, ideal for the separation and selective removal of water in a dry membrane state [8], are unstable in an aqueous solution [2]. The distance between GO nanosheets increases from ∼0.3 nm in the dry membrane state to 0.9–1.3 nm due to the effect of hydration, which reduces the selectivity. Small hydrated ions (K⁺, Mg²⁺, AsO₄³⁻) can permeate through the enlarged nanochannels [2].

rGO membranes, due to a smaller interlayer distance between rGO layers (0.34–0.37 nm), have a better selectivity for these purposes, but the water permeability of rGO membranes is significantly weakened due to a reduction of hydrophilic groups, which in some cases even leads to impermeable barrier films [9]. It has been
shown in [10] that rGO membranes obtained by GO reduction using hydroiodic acid have higher filtration ability and provide higher water permeability at a high rate of salt removal.

In [11], a new method for fabrication of an rGO membrane with high water permeability and a degree of retention of dissolved substances using poly-dopamine (PDA) is shown, which contains hydrophilic catechin groups and amino groups.

Our present work is devoted to the synthesis of composite rGO/PVDF membranes using a pulsed photon annealing (PA). This method, in contrast to traditional methods that use thermal heating, has several advantages. First of all, this is the simplicity of practical implementation and the ability to control the annealing process.

In this paper, a new method of separating the spectrum of photons using a glass IR filter was proposed, which significantly reduces the infrared heating of the samples. The features of water filtration through rGO/PVDF membranes were also studied.

2. Experimental

GO powders were prepared from graphite powder by the modified Hummers method [12]. To obtain reduced graphene oxide (rGO), the colloid GO suspension (3 mg of GO on 1 ml of H2O) was treated in an ultrasonic bath for 3 h. The resulting solution was mixed by a mechanical stirrer at 80 °C for 12 h. It led to the deposition of black powder of the rGO. After cooling to ambient temperature, rGO powder was sieved via filter with the subsequent reduction at 150 °C from 30 min to 120 min. A commercial GO suspension (Sigma-Aldrich [13]) was used for comparison.

rGO/PVDF membranes were prepared in an analogy [1] by a rGO suspension with the subsequent ultrasonic treatment within 30 min. GO was deposited on a polymeric PVDF membrane (Durapore Membrane Filter, 47 mm Hydrophilic PVDF membrane, pore size 0.22 μm) using vacuum filtration method (a two-stage vacuum pump of ROAIRVAC 1.5/3.0/6.0/9.0 R17300416 ROTHENBERGER, 500 Mbar) within 60 min, at ambient temperature with subsequent drying at 40 °C within 24 h. For comparison, similar GO/PVDF membranes were also used.

The GO and rGO suspensions and rGO/PVDF membranes were characterized by Fourier Transformation Infrared Spectroscopy (FTIR) by means of NicoletiS10 FTIR. Surface morphology and structure of rGO membranes were investigated by Scanning Electron Microscope Fe SEM Auriga Crossbeam 540 and with XRD (Bruker AXS D8 FOCUS).

The structure of rGO/PVDF membrane was studied by means of a high-resolution x-ray diffraction method with the use of the 4-circle x-ray diffractometer Bruker D8 DISCOVER with rotating copper anode running at 4 kV (CuKα1 radiation, λ = 1.54 Å). X-ray diffraction spectra were analyzed by means of the Bruker DIFFRAC plus software package.

Synthesis, physicochemical properties, and a structure package were analyzed by means of the EVA, TOPAS, and Find It software. EVA analyzed a qualitative composition of the sample with the use of a database of International Center for Diffraction Data [14] for Durapore Membrane Filter, 47 mm Hydrophilic PVDF membrane, a pore size of 0.22 μm, figure 1.

Find It allowed to search for CIF files (crystal information file) required for specifying x-ray diffraction patterns of the test samples in TOPAS. The crystallinity of the nanomaterial was characterized with XRD (Bruker AXS D8 FOCUS) with the use of a copper CuKα1 radiation source (λ = 1.54 Å). X-ray phase analysis of the ceramic samples was performed by means of a Bruker D8 Advance Vario x-ray diffractometer (copper CuKα1 radiation) with a Ge monochromator and a Lynx Eye position sensitivity detector in θ/2θ geometry with rotation and with the use of a Bruker D8 Advance x-ray diffractometer (copper CuKα1 and CuKα2 radiation) in θ/2θ geometry with rotation.

The filtration abilities of rGO/PVDF membranes were measured by using vacuum filtration pump (DA-15D, ULVAC KIKO, Inc.) with the pumping rate of 121 min⁻¹ and pressure of 6.65 kPa. pH of the water solutions 0.2 mol NaCl was measured by means of the pH meter (HANNA HI 2550 pH/ORP & EC/TDS/NaCl Meter). Permeability tests were carried out by means of two-unit L-shaped compartments. The conductivity meter was placed in the permeate part to record changes in ionic conductivity. The permeability test, based on measuring the passage of water through membranes, was carried out with using two-section L-shaped compartments. A controlled volume 20 ml of distilled water (DI) and 0.2 mol NaCl solution was used to filter and determine the time the liquid passed through rGO/PVDF membranes.

For improvement of adhesion of rGO/PVDF membranes were exposed to pulsed PA with halogen lamps of Quartz Xe-Halogen Lamp QTG-220-1300. The maximum power of nine lamps was 12 kW, the annealing time was varied from 1 s to 100 s. At the same time, the power of a light stream at a distance of 20 mm from the plane of lamps was 45 W cm⁻² [15]. The special glass IR- filter was used to avoid the thermal overheating of a sample at...
PA. The VERTEX-70V IR spectrometer with the HEPERION IR microscope was used to study the spectral features of the glass filter. The IR-filter didn’t transmit a part of IR-spectra, figure 2. Thereby the sample absorbed less energy and its temperature of heating has decreased.

The PA modes of rGO/PVDF membranes were chosen so that the GO layer was visible on the back side of the membrane substrate, figure 3.

3. Results and discussions

The nature of the increase in the intensity of D and G peaks in r-GO during GO reducing can be assessed by changes in the characteristic bands of the IR absorption spectrum, figure 4.

In figure 4 IR-spectra of GO suspensions are showed for different reduction times. The IR bands of the initial GO suspensions (0 min—black line) show two characteristic bands on the frequency range 3300 cm$^{-1}$ and 1600 cm$^{-1}$, which relate to the stretching vibrational bonds of hydroxyl OH– and carboxyl CO– groups [11]. When GO is restored, the absorption intensity of the 3300 cm$^{-1}$ and 1600 cm$^{-1}$ bands decreases, and new hydrogen-containing CH bands appear in the region of (500–900) cm$^{-1}$ and 1000–1571 cm$^{-1}$ and carbon-containing C–C bands of 1750–1800 cm$^{-1}$, table 1.

This is also observed in IR-spectra of the rGO/PVDF- membrane after photon pulse annealing PA, figure 5. In figure 5 are shown the IR-spectra before (blue) and after PA - the front side (red) and back side (black) of the rGO/PVDF membrane. The IR spectrum of a standard polymer PVDF-membrane located on the right. It can be seen that the IR spectrum of the rGO/PVDF- membrane before PA retains the characteristic IR-bands of...
The analysis of the IR spectra of GO and rGO (figure 4), as well as the IR spectra of the rGO/PVDF membrane after PA (figure 5), shows that the growths of carbon-containing C–C groups (1750 cm$^{-1}$) and C–H groups (1330 cm$^{-1}$ and 900 cm$^{-1}$). This suggests that in the process of GO reducing there is increased the carbon-containing C–C and C–H bonds due to the release of oxygen from OH hydroxyl and carboxyl CO groups, a graphitization of rGO are observed.

It is known [8] that the formation of C–H bonds increases the interfacial interaction between adjacent (in the plane) and adjacent (outside the plane) rGO sheets and this leads to a decrease in the interlayer space of rGO sheets [11]. In the absence or in a small amount of oxygen functional groups, rGO sheets aggregate more strongly due to the strong π–π-gravity and rGO are formed more defective [16].
It is seen on the SEM images of rGO/PVDF membranes. Figure 6 shows SEM images of the GO/PVDF membrane (6a) and rGO/PVDF membrane after 120 min of reduced, 6b.

It can be seen that the surface topology and the interlayer structure of the GO/PVDF membrane, which consists of the GO layer, are homogeneous. The GO layer consists of a larger number of (15–20) GO sheets. The thickness of the GO layer achieves the values of 1500–1700 nm, the thickness of the GO sheets is about 70–100 nm, figure 6(a). The surface of the rGO/PVDF membrane, consisting of the rGO layers, reduced at 160 °C for 120 min, is not uniform. The thickness of the rGO layer is reduced to 1200 nm; the thickness of the rGO sheet is approximately 60–80 nm, figure 6(b). During long-term (120 min) reduction, the rGO layers strongly aggregate and form more defects, and accordingly, the surface of the rGO/PVDF membrane become more defectively. A decrease in the functional OH– and CO– groups leads to an increase in the hydrophobicity of rGO [1] and, therefore, sheets of reduced rGO, unlike graphene oxide sheets, become hydrophobic and form irreversible agglomerates in the form of graphite in aqueous solutions. That is, the presence of rGO allows one to modify the surface of the rGO/PVDF membrane and further increase its hydrophobicity.
The research of the structure of rGO/PVDF membranes by means of XRD showed that PA leads to increasing of their crystallinity, figure 7.

XRD peaks of PVDF and rGO/PVDF are taken from the database, figure 7. On XRD peaks GO reflection planes are specified. The specified planes of GO reflection demonstrate crystallinity of structure. It is clear that with annealing the intensity of XRD peaks as PVDF (peaks about 20 degrees) and GO increases (peaks in the area of 27–85 degrees). Figure 7 shows the XRD spectra of a PVDF membranes and b) rGO/PVDF. The analysis of x-ray diffraction spectra showed the appearance of different diffraction peaks of GO (200), GO (220), GO (222), GO (400), GO (420), GO (422). The occurrence of diffraction peaks from different planes of GO demonstrates that the GO layer consists the graphene oxide flakes with different orientations.

The XRD spectrum on figure 7(a) shows the that the increase of annealing time lead to an increase of the diffraction peaks intensities (from GO8 to GO11) by improving the perfection of the crystal structure of GO flakes. It demonstrates that PA increases the crystallinity of rGO/PVDF membrane structure.

The filtration results showed that the modification of standard PVDF membranes with additives of both GO and r-GO, improve their filtration ability \( f_s \) and permeability \( \varepsilon \) compared to a standard method, table 2.

Filtration results showed that the modification of standard PVDF membranes with both GO and rGO additives improves their filtration abilities \( f_s \) compared to standard PVDF membranes, see e.g. in table 2. After filtration, the salt content decreases to the level of distilled water. The best salt retention is observed for the rGO/PVDF (30 min) membrane, reduction time \( t_r = 30 \) min. At increase of the reduction time \( t_r \) to 60 min, 90 min and 120 min, the filtration ability \( f_s \) of rGO/PVDF- membranes decreased. It is explained that at a \( t_r \) increase, the amount of oxygen (hydroxyl OH– and carboxyl CO–) groups there decreased and due to these the hydrophobicity and smoothness increased [1, 10]. It leads to a higher rate of permeation of water molecules through the interlayer nanochannels rGO, showing a higher permeability \( \varepsilon \). An increase in permeability \( \varepsilon \) leads to a decrease of the filtration ability \( f_s \) (cf table 2, columns 3 and 4). As can be seen, the \( t_r \) growth leads to a \( t_p \) decrease, where the permeation time of water via the rGO/PVDF membranes and accordingly, \( \varepsilon (120 \text{ min}) > \varepsilon (90 \text{ min}) > \varepsilon (60 \text{ min}) > \varepsilon (30 \text{ min}) \). Such an acceleration of water passage through the rGO membranes has been observed in [1, 10] and is explained by the presence of reduced hydrophobic rGO regions, which enhance the sliding velocity due to the hydrophobicity and smoothness of the interlayer nanochannels rGO/PVDF.

![Figure 7. XRD patterns of PVDF (a) and rGO/PVDF (b): pristine PVDF (GO8, black), annealing at 8 s (GO10, red), and at 11 s (GO11, blue).](image)

| Membrane type               | \( f_s \) (pH) | Salt solution | Distilled water | Salt solution |
|----------------------------|----------------|---------------|----------------|---------------|
| Initial salt solution      | 9.80           | 40            | 51             |               |
| PVDF                       | 7.78           | 23            | 28             |               |
| GO/PVDF                    | 7.56           | 30            | 88             |               |
| r-GO/PVDF (30 min)         | 7.02           | 24            | 86             |               |
| r-GO/PVDF (60 min)         | 7.07           | 24            | 31             |               |
| r-GO/PVDF (90 min)         | 7.09           | 17            | 25             |               |
| r-GO/PVDF (120 min)        | 7.63           | 17            | 25             |               |

Table 2. Filtration results.

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In addition to hydrophobicity and smoothness of nanochannels, authors of [1] used the theory of sliding flow in carbon nanotubes (CNTs) [16], in order to explain their result. According to this model, an acceleration of flow rate of water in CNT [3] is possible because of the decrease of activation energy of shear viscosity of the liquid in nanoscale channels. According to the computer modeling mechanisms of water molecules movement in CNT is explained by the slip flow theory [16], where the flow enhancement is related to the slip length, hydrophobicity, smoothness, and diameter of the nanotubes [17].

The water flow rate increases with CNT diameter decrease that is caused by smaller surface interaction with water and decrease of activation energy of shear viscosity of the liquid [16]. The dependency of water flow rate on CNT diameter shows that with the reduction of CNT diameter water flow rate increases [18].

Water flow rates in planar graphene nanochannels via rGO membranes are faster, not only due to the strengthening of hydrophobicity and smoothness of nanochannels but also with the decrease in activation energy of shear viscosity of the liquid [16].

4. Conclusion

The fabrication of efficient rGO/PVDF membranes are demonstrated using graphene oxide nanocrystallites rGO as inclusions on the surface in standard polymeric PVDF membranes. Composite rGO/PVDF membranes consist of a larger number (15–20) of rGO layers, the thickness of the rGO layer reaches 1500–1700 nm, the thickness of one rGO sheet is 70–100 nm, each rGO sheet consists of rGO flakes of different orientations. rGO/PVDF membranes have shown the best filtration effectiveness as compared to the standard polymeric PVDF membranes. The dependence of the flow rate of water transportation via interlayer nanochannels of rGO/PVDF membranes on the reduce time of rGO has been observed. An increase in the reduction time of rGO leads to an increase in the rate of water permeation through rGO/PVDF membranes due to a decrease in the activation energy of shear viscosity of water in rGO nanochannels. Since the water flow rate depends on the degree of reducing of the rGO membrane, an optimum ratio between the level of reduction and the rate of permeability of water through the membrane has been obtained. The rGO membrane treated at 160 °C for 30 min with a small amount of unreduced GO shows the smallest penetration of Na/Cl ions, while the rGO membrane (120 min) showed the maximum rate of passage of water.

Application of pulsed photon annealing PA facilitated fabrication of stable rGO/PVDF membranes. PA leads to an increase in the crystallinity of the rGO/PVDF membrane structure, which depends on the duration of PA. An increase in the duration of the annealing pulse leads to an improvement in the perfection of the crystal structure of rGO flakes.

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