Antifouling enhancement of polysulfone/TiO$_2$ nanocomposite separation membrane by plasma etching

Z Chen[1], C Yin[1], S Wang[1], K Ito[2], Q M Fu[1], Q R Deng[1], P Fu[1], Z D Lin[1] and Y Zhang[1]

[1]Hubei Key Laboratory of Plasma Chemical and Advanced Materials & Department of Material Science and Engineering, Wuhan Institute of Technology, Wuhan, 430073, China

[2] National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki 305–8565, Japan

E-mail: zhezchen@gmail.com

Abstract. A polysulfone/TiO$_2$ nanocomposite membrane was prepared via casting method, followed by the plasma etching of the membrane surface. Doppler broadened energy spectra vs. positron incident energy were employed to elucidate depth profiles of the nanostructure for the as-prepared and treated membranes. The results confirmed that the near-surface of the membrane was modified by the plasma treatment. The antifouling characteristics for the membranes, evaluated using the degradation of Rhodamin B, indicated that the plasma treatment enhances the photo catalytic ability of the membrane, suggesting that more TiO$_2$ nanoparticles are exposed at the membrane surface after the plasma treatment as supported by the positron result.

1. Introduction

Separation membranes are widely applied to the water filtration. During the filtration process for organic wastewater treatments, a fouling on the membrane surface due to the adsorption of organic pollutants is a major issue, which reduces the water flux, increases the energy consumption, and shortens the service lifetime of the membrane. According to the conventional filtration blocking theory [1], the fouling mechanism includes the following models: (1) standard blocking (gradual pore constriction), (2) complete blocking (sealing of pore entrances), (3) intermediate blocking (sealing and accumulation on membrane surface), and (4) cake filtration. All the above models indicate the membrane fouling is related to the accumulation of foulants on the membrane.

Introducing photo-active nanoparticles, capable to transfer the organic foulant to CO$_2$ and H$_2$O, is a promising way to provide a photo catalytic ability to the membranes. Yang, et al. have reported that polysulfone/TiO$_2$ composite membranes exhibit excellent water permeability, hydrophilicity and good antifouling ability [2]. For the prepared membrane, most TiO$_2$ nanoparticles, responsible to the photo-catalytic antifouling ability, are wrapped in the bulk. Thus, the antifouling ability of the membrane may be enhanced by exposing more TiO$_2$ nanoparticles at the membrane surface.

In this work, a polysulfone/TiO$_2$ nanocomposite membrane was prepared via casting method, followed by the plasma etching of the membrane surface. The difference in photocatalytic activity between the two membranes was tested in order to examine the effect of the plasma treatment on the antifouling ability. Positron annihilation γ-ray spectroscopy was employed to probe depth profiles of the nanostructure for the as-prepared and modified membranes. The obtained results are discussed in comparison with the antifouling property of the membranes.

2. Experimental

TiO$_2$ nanoparticles with a nominal average size of ~30 nm were purchased from Degussa. The nanoparticles were dispersed into N-methyl-2-pyrrolidinone (NMP) to obtain a 1-wt% suspension, followed by dissolving a proper amount of polysulfone in the suspension with stirring and ultrasonic vibration to obtain a homogeneous suspension with 19-wt% polysulfone and 1-wt% TiO$_2$. The prepared suspension was then poured at room temperature onto a glass plate with a 800-μm-thick blade. After exposing to air for 30 s, the suspension on the glass was immersed in a water bath at ~25 °C for 1 day to remove the remaining solvent from the membrane.

A plasma treatment was performed in a RF-plasma reactor (YZD08-2A) purchased from Tangshan Yanzhao technical institute. The RF discharge was excited with plain parallel electrodes placed in about 50 mm distance. The treatment with placing the membrane on one electrode was carried out for 5 min with an RF power of 80 W and an operating argon pressure of ~ 10 Pa.

Positron annihilation γ-ray spectra for the membranes were measured with a ^{22}Na-based, magnetically-guided positron beam at AIST. The line-shape S parameter was determined as the ratio of the counts appearing in the central region (510.3 keV–511.7 keV) to the total counts of the 511 keV annihilation photo peak (506.8 keV–515.2 keV) for each spectrum recorded with a high-purity Ge detector. The mean positron implantation depth z [nm] is estimated by the following formula [4]

$$z = \frac{40}{\rho}E^{1.6} \tag{1}$$

where E is the incident positron energy in keV and ρ is the density of the measured membranes in g*cm^{-3}.

The photocatalytic activities of the present membranes were evaluated by monitoring the degradation due to the irradiation of a 300-W Xe light to a rhodamin B (RhB) solution which was obtained by immersing a 2-cm-2-cm-sq. membrane sheet into 500-ml RhB solution. The distance between the Xe lamp and the RhB solution was about 15 cm. The reaction apparatus for the irradiation was put in a water bath at ~30 °C. After stirring in darkness for 30 min to attain the adsorption-desorption equilibrium, the Xe lamp was turned on. A 2-ml solution was sampled every 30 min, followed by quantifying the remained RhB in the solution using a UV-vis spectrometer. A blank experiment was carried out without the photocatalyst, as a result, the photolysis effect for RhB was confirmed to be negligible, which ensures the stability of RhB.

3. Results and Discussion

3.1. Positron annihilation γ-ray spectroscopy

Figure 1 shows the variation of the S parameter for the membranes before and after plasma treatment as a function of positron incident energy E. For both the membranes, the $S(E)$ curves exhibit similar shape, namely S increases with increasing E from 80 eV to 2 keV, and it reaches a flat stage at $E > 2$ keV. In comparison with the untreated membrane, the $S(E)$ curve for the treated one exhibits a distinct decrease in the S values at the respective E less than 1 keV, corresponding to a mean implantation depth around 40 nm.

For polyolefin systems, S is generally related to the Ps formation probability and the momentum of the electrons belonging to the constituents of the polymer chains. Both of these

two factors are significantly influenced by the chemical structure of the material. According to the spur reaction model [5], the Ps formation is partially inhibited by positron trapping and annihilation with polar groups in the matrix reducing the S parameter. In light of this, the lower S at the near-surface region for the present modified membrane suggests inhibition of the Ps formation due to polar groups or more metal oxide nanoparticles at the near-surface region. Moreover, the difference in S between the treated and untreated membranes becomes significant at $E < 1$ keV, corresponding to a mean implantation depth of < 40 nm. This indicates that the chemical structure of the treated membrane at the near-surface region is different from that for the untreated one.
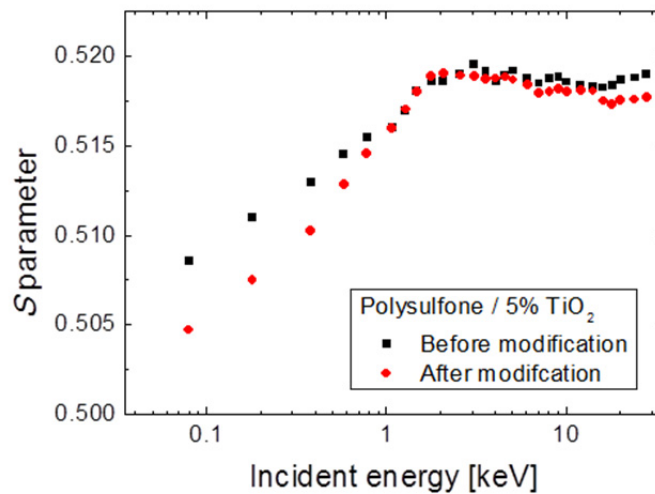

Figure 1. Variation of S parameter for the samples (membrane as obtained and membrane after modification) as a function of positron incident energy.

3.2. Photo catalytic ability for aqueous RhB

Figure 2 shows the variation of the relative RhB concentration C/C_0 in the immersing solutions for the membranes before and after the plasma treatment as a function of Xe irradiation time. C/C_0 for both the membranes monotonously decreases with increasing the irradiation time, in which the reduction rate of C/C_0 for the treated membrane is significantly higher than that for the untreated membrane, This indicates that the plasma treatment effectively enhances the photocatalytic activity, implying that more TiO$_2$ nanoparticles are indeed exposed on the membrane surface due to the plasma etching, as expected by the result from the S parameter measurements.

The cycling performance of the treated membrane was further investigated to evaluate the photocatalysis stability. Figure 3 shows the repetition test of the photocatalytic activity for the treated membrane. As shown in the figure, even after several cycles for the photo degradation test of RhB, the treated membrane does not exhibit any significant loss of photo catalytic activity, indicating that the polysulfone/TiO$_2$ membrane after the plasma treatment is stable enough for the photocatalytic oxidation of the pollutant molecules.
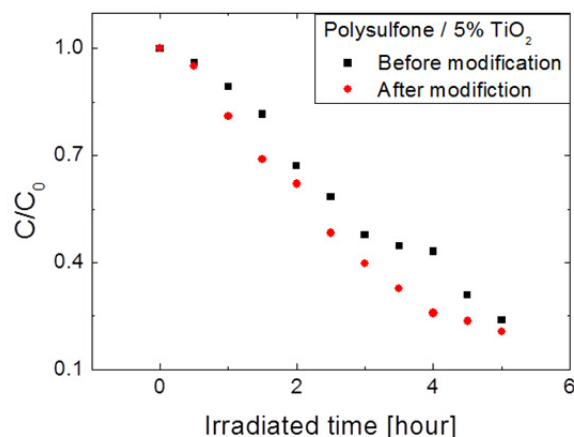
Figure 2. Variation of the relative RhB concentration in the immersing solutions for the membranes before and after the plasma treatment as a function of Xe irradiation time.
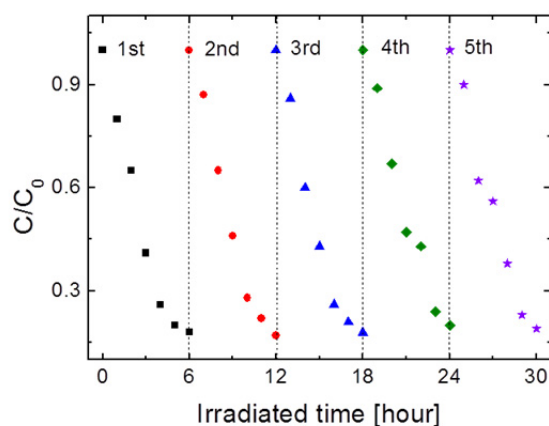

Figure 3. Repetition test of the photocatalytic activity for the treated membrane.

4. Summary

TiO$_2$ nanoparticles were introduced into a polysulfone membrane to attain the photocatalytic activity for antifouling, and the membrane near-surface was etched by the plasma treatment. A comparison of the photo degradation of RhB between after and before the plasma treatment showed that the photocatalytic activity is effectively enhanced, implying that more TiO$_2$ nanoparticles are   exposed on the membrane surface, as expected by the result from the *S* parameter measurements.

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