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Novel nanohybrid polysulfone membrane embedded with silver nanoparticles on graphene oxide nanoplates

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HIGHLIGHTS

- Graphene oxide (GO) as nanoplates synthesised using natural graphite powder.
- Polysulfone membranes have been embedded with silver nanoparticles on GO nanoplates.
- Improved hydrophilicity and permeability for all Silver-decorated GO wt% additions.
- Membranes exhibit superior antibacterial properties.

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ABSTRACT

Combining silver nanoparticles with graphene oxide (GO) nanoplates may provide a more uniform distribution of silver in membranes. GO nanoplates were synthesised using natural graphite powder according to Hummers method. Silver-decorated GO was prepared by reducing silver nitrate in the presence of aqueous sodium borohydride solution. X-ray diffraction (XRD), transmission electron microscopy (TEM), and Fourier transform infrared (FTIR) spectroscopy were used to investigate the silver-decorated GO. The membranes were fabricated by the wet-phase inversion method and were mixed with different amounts (0.00–1.00 wt%) of silver-decorated GO. Membrane properties such as hydrophilicity, pure water flux, and rejection were enhanced for all of the nanohybrid membranes. The optimum amounts of silver-decorated GO for optimum membrane properties was 0.5 wt%, which resulted in a lower contact angle as well as higher flux and porosity. The nanohybrid membranes also showed excellent antibacterial properties, which could delay or prevent the formation of biofouling on the membrane surface and provide an opportunity for new applications in the future.

1. Introduction

The advent of nanotechnology for various applications has been increasing rapidly and intensively. Membrane technology is not an exception to this development. Metallic and non-metallic nanoparticles have been embedded in membrane matrices to obtain new nanohybrid membranes with enhanced performances such as higher water permeability, better surface hydrophilicity or wettability as well as higher thermal and mechanical stability. Reducing the surface hydrophilicity of the membrane has become one of the main objectives of membrane modification, as it has shown less fouling potential [1]. However, hydrophilic surfaces are exposed to a higher bacterial growth potential [2], which makes them undesirable in terms of biofouling properties. The solution to this problem could be a new nanohybrid material that possesses a synergistic effect from the properties of two different nanomaterials. Herein, we report a novel type of membrane using polysulfone (PSF) incorporated with silver-decorated graphene oxide (GO). The use of silver with GO as nanoplates offers significant improvement in terms of providing a more homogenous distribution of silver across the membranes while enhancing other properties, especially the membrane antibacterial effect.

PSF is one of the most attractive materials to be used in membrane fabrication, owing to its excellent mechanical properties and higher water flux in comparison to nylon and polyvinylidene fluoride (PVDF) membranes. However, the surface of the PSF

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membrane is slightly hydrophobic in nature, which possibly reduces its surface wettability or self-cleaning effect for prolonged application [3]. There have been a number of works trying to reduce the hydrophilicity of the PSF membranes by embedding metallic or non-metallic nanoparticles. It has been reported that the addition of TiO_2 has successfully enhanced the mechanical strength of the membranes up to 50%. At the same time, the membrane hydrophilicity, pore number, antifouling ability and permeability displayed significant enhancements [4]. Besides, a certain amount of polyvinyl alcohol (PVA) and SiO_2 nanoparticles have been incorporated into the matrices of PSF membrane, which contributed to the enlargement in membrane pore size and thus increased the water permeability [5]. On the other hand, the addition of Fe_2O_3 in a parallel magnetic field contributed to the formation of a membrane with "lamellar macrovoids", which showed good enhancement in anticompaction as well as increased flux and rejection [6]. It also has been reported that, when an optimum amount of clay was incorporated into the matrices of PSF membranes, the mechanical structure, pure water flux as well as surface hydrophilicity of the PSF membranes was successfully improved [7]. Addition of ZnO nanoparticles to the PSF membrane also exhibited the same effect as clay. Recently, the control of ZnO nanoparticle size has been reported as the main criterion to improve membrane properties such as hydrophobicity, pore number and permeability [8]. There have also been a number of reports on the antifouling and antibacterial properties of Ag nanoparticles incorporated within the PSF membrane [8]. However, inorganic materials, especially those that are nano-sized, are not always spared from a common problem in which the nanoparticles cannot be homogenously dispersed in the membrane matrix and even form aggregates when the concentration of particles is relatively high. As is well known, the dispersion of inorganic particles and the compatibility between inorganic and polymer phases has a substantial effect towards the membrane properties. The membrane performance would deteriorate significantly when the aggregation of inorganic particles occurs. Thus, the aggregation of nano-sized inorganic particles in the polymer matrix should be minimised in order to develop a composite membrane with a high performance [9].

One of the main problems with nano-sized materials is caused by the difficulty in producing a homogenised dispersion in the matrix of a membrane. Agglomeration is a common phenomenon at higher concentrations of nanoparticles. This may lead to unwanted membrane characteristic such as weak polymer structure and pore blockage [10]. Therefore, there is a need for a new approach to improve homogenisation and reduce the agglomeration of nanoparticles in order to synthesise a high-performance membrane. Combining the nanoparticles with nanoplates such as GO may be one of the solutions to this problem.

Recent studies have shown that graphene and GO may be a revolutionary addition to the nanomaterial family [11]. Attention has been drawn towards these wonder materials as new polymer nanofillers, owing to their unique properties such as a 2D carbon nanostructure, good thermo-mechanical stability and high specific surface area [12]. Polymers such as PVDF, nylon 6-6, PVA, and PSF [13] have been reported to exhibit better thermal and mechanical properties after the addition of graphene or GO into their matrices. These enhanced properties encouraged the employment of graphene and GO as nanofillers in nanohybrid membranes. Hydrophilic groups such as the hydroxyl, carbonyl and carboxyl groups found in GO make it one of the best candidates for membrane modification purposes. Zhao et al. [14] have reported that the addition of graphene to the PVDF membrane improved the surface hydrophilicity, pure water flux and solute rejection capability of the membrane. On the other hand, the incorporation of GO into the PES membrane has been investigated by Zinadini et al. [15], in which their membranes showed dramatic improvement in properties such as porosity, pure water flux, antifouling properties and rejection. PVA–GO membranes fabricated by Wang et al. [16] for the pervaporation separation of toluene/*n*-heptane mixtures demonstrated significant improvements in terms of the mechanical and thermal properties.

Hybrid nanomaterials that could be developed together with GO contributed to a more interesting research area. These materials are characterised by a synergistic effect between GO, as the nanoplates, incorporated in different kinds of nanoparticles. For instance, Stengl et al. obtained an advanced photocatalytic material using a TiO_2–GO nanohybrid [17]. Chen et al. [18] also demonstrated the improved photocatalytic property of a ZnO/GO composite material. A superhydrophilic coating with a contact angle of 5° was exhibited by a SiO_2 and GO nanohybrid, owing to their sandwich structure when the SiO_2 was densely and evenly covering the GO surface [19]. In addition, Das et al. prepared GO decorated with silver nanoparticles, which showed good antibacterial properties, using Kirby–Bauer antibiotic strength measurements for *E. coli* [20].

As these GO nanoplates can be uniformly decorated with nanoparticles, the agglomeration problem can possibly be resolved when used to produce a nanohybrid membrane. The aim of this work was to study the fabrication of a novel membrane using PSF and silver-decorated graphene nanoplates. Silver-decorated graphene could improve overall membrane performances including their antibacterial properties and the surface hydrophilicity of the membrane. The synergistic influence of silver-decorated graphene towards the membrane performances was shown through characterisation, using pure water flux, rejection, contact angle, field-emission scanning electron microscopy (FESEM) imaging and antibacterial testing.

2. Materials and methods

2.1. Materials

Extra-pure, fine graphite with a particle size of less than 50 μm was obtained from Merck Co. Potassium permanganate ($KMnO_4$) and sulfuric acid (H_2SO_4) (98 wt%) were supplied by Accot Malaysia. PSF was received in pellet-form from Sigma. *N*-Methyl-2-pyrrolidone (NMP) from Sigma was used as the solvent. Albumin from bovine serum (98%, M_W 69 KDa) was received from Sigma in powder form.

2.2. Synthesis of GO

GO was synthesised using natural graphite powder according to Hummers method [21]. Graphite powder (5 g) and sodium nitrate (2.5 g) were added to a round-bottom flask together with concentrated H_2SO_4 (115 mL). Then, the mixture was stirred for 30 min in an ice bath until it reached a temperature of 10 °C. Next, $KMnO_4$ (15 g) was added gradually under continuous stirring. The mixture

Table 1
Membrane designation based on polymer-to-nanoplate ratio.

Sample	Ag-decorated GO concentration [wt%]	PSF:NMP:Ag-decorated GO
M1	0	1:5.56:0
M2	0.1	1:5.56:0.001
M3	0.3	1:5.56:0.003
M4	0.5	1:5.56:0.005
M5	0.8	1:5.56:0.008
M6	1	1:5.56:0.01