Monolayer graphene transfer onto polypropylene and polyvinylidenedifluoride microfiltration membranes for water desalination

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HIGHLIGHTS

- We transfer monolayer CVD graphene onto commercial polymeric membranes (polypropylene & polyvinylidenedifluoride).
- We examine the quality of transferred graphene by SEM and KCl ionic transport through graphene/polymeric membrane composites.
- We seal defects (tears and cracks) within graphene layer by interfacial polymerization (IP) of Nylon 6,6.
- % ion blockage increases with interfacial polymerization (after defect sealing).
- % ion blockage enhances when IP process optimized in terms of constituent's concentration and process duration.

GRAPHICAL ABSTRACT
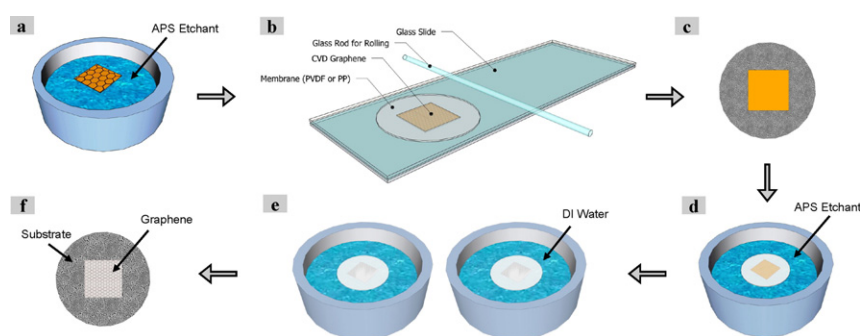
ABSTRACT

Transfer of graphene to porous substrates with minimal defects is important for the fabrication of graphene membranes for water desalination. Here we investigated the transfer of monolayer chemical vapor deposition (CVD) graphene grown on copper (Cu) onto two commercial microfiltration membranes, namely polypropylene (PP) and polyvinylidenedifluoride (PVDF). The graphene layer was attached to the target substrate surface by sandwiching the Cu–graphene-membranes, followed by wet etching of the Cu substrate leaving behind the monolayer graphene on the membrane surface. SEM characterization indicated good transfer and surface coverage, but revealed the existence of defects within graphene layer which originated from the transfer process. Transport characteristics of the resulting graphene membranes were investigated by diffusion of potassium chloride (KCl) ions using a Side-bi-Side diffusion cell, graphene–PP membrane blocked 57% of KCl ions whereas graphene–PVDF membrane blocked 40% of the ions suggesting the presence of defects within graphene. An attempt to seal defects was carried out via interfacial polymerization (IP) of Nylon 6,6 into the defects using a Franz Cell, allowing sealing of defects and increasing KCl ion blockage to 67% for both membranes. The IP process was then optimized to seal the defects more effectively, which increased the ion blockage further to 84% for graphene–PP membranes.

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1. Introduction

Resistance-free ultrafast transport of water molecules through a membrane while blocking all other ionic species is a point of interest for the reverse osmosis (RO) based sea and brackish water desalination industry nowadays. Despite considerable improvement efforts in the recent past, the current state-of-the-art RO membranes do not offer the desired high levels of permeance and are prone to fouling [1–6]. The thickness of the active (selective) layer of the state-of-the-art polymeric membranes limits the permeability, whereas fouling causes a further flux decline with time and also lowers the membrane's salt rejection capacity [6–8]. To realize the ultrafast permeance with minimal resistance to flow, the membrane's active layer needs to be as thin as possible and to maintain the operating costs at bay. Effective solutions to membrane fouling must also be found. Among various approaches being explored which target the permeability and fouling issues, an emerging approach is to find alternative membrane materials which are inherently free from the limiting factors which hinder the ultrafast water transport through the membranes [9–12].

One such promising material is graphene [13,14], which not only offers exceptional chemical [15], thermal [16] and mechanical [17,18] stability, flexibility [19] and low fouling characteristics [10,20], but most notably is the thinnest possible membrane with its one atom thickness acting as the separation (active) membrane layer [9]. Pristine graphene, however, is almost totally impermeable even to the helium atoms [7, 18], and the key for its use as a separation membrane, especially for RO process, is to create appropriately-sized pores for selective passage of only water molecules while rejection of other ionic species [21–23]. Synthesis of membranes containing one atom thick graphene layer with a tailored pore size that would allow such ultrafast water permeability is an area of intensive research around the globe [21,22,24–26].

A key step in the fabrication of efficient graphene-based separation membrane is the careful transfer of graphene onto a suitable substrate that can provide the necessary support to its single atom thick layer [22]. Polymeric ultra- and nano-filtration membranes are best suited to act as the support substrates since graphene suspended over large pores is fragile, but is predicted to withstand remarkably high pressures when suspended over small pores, such as those of ultra- or nano-filtration membranes [19,27–29]. However, transfer of a graphene monolayer to a polymeric membrane substrate is extremely challenging. Despite recent advances in technology, known methods used to transfer graphene result in the introduction of large defects (tears, holes, and cracks) in the graphene layer [22]. These defects must be plugged and sealed to block solute permeation through the defects and to produce an impervious graphene/polymer composite membrane prior to introducing rightly sized-pores to convert it to a workable separation membrane. Interfacial polymerization can be adopted to seal the defects where suitable monomers can be made to meet interfacially inside the defects and polymerize to plug the defects [24].

The quality of the graphene transfer to a polymeric substrate largely depends on the surface characteristics of the substrate [22,30]. Most important among these are the substrate pore size, surface roughness, and surface wettability. A smooth surface is needed to provide good and conformal adhesion of the graphene monolayer onto the substrate [31]. Small pore size would render sound mechanical support to graphene domains that may otherwise be poorly supported and tear and crack if the substrate pores are large. High hydrophobicity is needed to discourage penetration of the etchant solution between the graphene and membrane substrate and deleteriously attack the graphene layer and deteriorate its quality [22].

In the present work, monolayer graphene grown over Cu foil via CVD was transferred onto polypropylene (PP) and polyvinylidenedifluoride (PVDF) commercial microfiltration membranes. The quality of transferred graphene monolayer was examined as a function of substrate pore size, surface roughness, and wettability. Diffusion studies were carried out using potassium chloride (KCl) solution. Defects (tears and cracks) originating from the transfer process were sealed by interfacial polymerization (IP) of Nylon 6,6. Finally, the concentration of the monomer solutions used in IP process and the IP reaction time were optimized to obtain the best defect sealing conditions to maximize the ion blockage. This work is a step forward toward the graphene membranes that could be used as desalination membranes.

2. Materials and methods

2.1. Materials

Monolayer graphene grown on a copper (Cu) substrate (25 μm thick Cu foil) was purchased from ACS Material Company, USA. The graphene was grown using low-pressure CVD process (CVD graphene grown onto Cu shows better quality and coverage when compared with the other catalysts such as Ni (Ref)). Raman spectroscopy was performed and confirmed the coverage of monolayer graphene over Cu substrate, see Fig. S1.

Polypropylene membranes (100 nm pore size) and polyvinylidenedifluoride membranes (20 nm pore size) which were used as substrates were procured from Sterlitech Corporation, USA, and Novamem Advance Separations Company, Switzerland, respectively. The characteristics of these substrates are reported in Table 1. The etchant used to dissolve and remove Cu was prepared by mixing 5% (wt./vol.) of ammonium persulfate (APS) (Eurostar Scientific Ltd) with de-ionized water. Potassium chloride (KCl) used for diffusion studies and hexane used for interfacial polymerization were purchased from Merck, Germany. Hexamethyldiamine, Adipoyl chloride and Texas red®-X, Succinimidyl Ester, and mixed isomers dye were supplied from Fluka Chemicals, Sigma-Aldrich, and Life Technologies Company, USA, respectively.

2.2. Transfer process

Graphene transfer process onto both PP and PVDF membranes was adopted from O'Hern et al. [22], which is simply a modification of the direct transfer method developed by Regan et al. [32]. The process as shown in Fig. 1, begins with removal of graphene from one side (which is in fact deposited on both sides of the Cu foil during graphene production) by floating a 1×1 cm^2 piece (graphene/Cu) over the etchant (APS) for 5–7 min. This was followed by dipping it in de-ionized water multiple times to remove any entrapped etchant. This step provides a monolayer graphene on one side of Cu foil. The graphene monolayer was attached to the target substrate membrane (PP or PVDF) by sandwiching them with the graphene/Cu between two glass slides and roll pressing with a glass rod (see Fig. 1b). A gentle pressing was used to allow conformal graphene attachment to the substrate surface while as minimizing damage to the graphene monolayer (see Fig. 1c).

The transfer process was then completed by etching away Cu using the same APS etchant (Fig. 1d) leaving behind well-attached graphene monolayer on the target membrane. Graphene membrane was then passed through two de-ionized water baths for complete removal of the etchant and finally the membrane samples air-dried (see Fig. 1f).

Table 1
Characteristics of as-received PP and PVDF membranes.

Membrane	Pore size (nm)	Thickness (μm)	Surface wetting	pH range	Max. temperature
PP	100	75–110	Hydrophobic	1–14	180 °C
PVDF	20	20	Hydrophobic	0–12	120 °C