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Functional graphene nanosheets: The next generation membranes for water desalination

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HIGHLIGHTS

- Graphenes are exceptional materials for the next generation water separation membranes.
- Graphenes prove ultrafast permeance, excellent mechanical strength and precise ionic sieving.
- Modified NPG and GO membranes showed exceptional antifouling properties.
- Need full understanding of the transport mechanism of NPG and GO membranes
- Mechanical performance of fully wetted NPG and GO membranes must be addressed.

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ABSTRACT

Membrane desalination and water purification technologies have become important energy-efficient means to secure fresh water resources around the globe. Among the significant recent advancements in the design and development of new membrane systems is the use of graphenes. Graphenes have offered a novel class of mechanically robust, ultrathin, high-flux, high selectivity, and fouling resistant separation membranes that provide opportunities to advance water desalination technologies. The facile synthesis of nanoporous graphene (NPG) and graphene oxide (GO) membranes opens the door for ideal next-generation membranes as cost effective and sustainable alternative to the long-existing thin-film composite polyamide membranes for water purification applications. In this review, we highlight the structure and preparation of NPG and GO membranes. We also discuss the recent experiments, computer simulations and theoretical models, addressing the unique mechanical properties, ion selectivity, and possible transport mechanisms through NPG and GO membranes. We will focus on the fabrication and functionalization schemes of graphene oxide membranes. Particular emphasis is on the antifouling properties of the NPG and GO modified membranes. We believe this review will open new avenues for new innovations and applications of NPG and GO in water desalination and treatment.

Contents

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1. Introduction

The increasing scarcity of freshwater sources across the globe has urged the need to develop alternative water supplies, including seawater desalination, reuse and recycling of wastewater and storm water [1, 2]. Membrane-based desalination techniques, mainly reverse osmosis (RO), are currently considered as more environmentally friendly and energy-efficient than that of thermal desalination methods such as multistage flash and multiple-effect distillation. However, these technologies suffer from low desalination capacity and high capital costs. For example, RO consumes ~2 kWh m^{-3} for a 50% recovery with a theoretical minimum energy of ~1 kWh m^{-3}. Moreover, conventional polymeric membranes currently used in RO plants are prone to fouling, suffer from flux decline under high pressure, undergo rapid degradation, and have low tolerance to high temperature, acids/alkaline, chlorine, and organic solvents [3]. This has urged the need for developing novel membranes which can reduce the energy consumption of the RO process by showing high water permeability coupled with high salt rejection capacity [4,5].

The ideal membrane should provide higher flux, higher selectivity, improved stability, and resistance to chlorine and fouling. Also it should be as thin as possible and mechanically robust to maximize permeability, chemically inert and must retain a high salt rejection rate throughout its service life [6]. Recently, nanostructures such as zeolites, metal organic frameworks, ceramics and carbon based materials have attracted considerable attention as alternative membrane materials to replace polymeric membranes due to good chemical resistance, high flux, and high rejection rates [4].

On the other hand, zeolite membranes have failed to realize economical fabrication on a large scale due to manufacturing cost, reproducibility and defect formation [7]. Also, ceramic membranes are costly and very brittle under high pressure which limits their practical applications in membrane technologies. Although it is possible to fabricate high-flux and high selectivity membranes from carbon nanotubes (CNTs), it is currently difficult to synthesize highly aligned and high density CNTs with large lengths. CNTs remain an active area of research for membrane technologies but costs and operational issues have greatly hindered the development and integration of CNTs into large area membranes [8].

Recently, graphene based materials have attracted great interest for their potential exploitation in water desalination and purification membranes. This can be attributed to their unique properties including distinctive structural characteristics [9], high mechanical strength [10] and negligible thickness [11]. The advancement in molecular simulation of graphene family opens the door for their potential contribution in developing novel membrane desalination technologies. Graphene's unique electronic properties, high tensile strength and impermeability to small molecules is now a well determined fact [12–16] and these have been utilized to construct extremely thin membrane with size tunable pores (for molecular sieving) allowing for high flux. Graphene nanosheets display ideal chemical and physical properties in the desalination process. Despite its negligible thickness, membranes made of graphene exhibit adequate mechanical strength, capability of functioning under higher pressures that is superior to conventional polymeric RO membranes currently in circulation [11,17].

Several simulation studies have identified nanoporous graphene (NPG) structures among the most promising membrane materials that can provide high water flow rates and high salt rejection as a function of nanopore morphology [17]. On the other hand, these hypotheses are based on a single layer of graphene sheet which is difficult to assemble in the real world [18].

Thus, despite the great theoretical promise, there remains a major challenge to achieve cost effective and scalable manufacturing of large NPG membranes displaying the required subnanometer pores and narrow size distribution while preserving graphene's intrinsic structural integrity. To this end, continuous efforts are in quest to identify affordable and scalable NPG frameworks while maintaining the desired molecular and ion sieving performance. The evaluation of NPG performance and feasibility needs to be carried out through a detailed study of its salt rejection and water flux. In addition, its mechanical durability and chemical stability need to be investigated [8]. Alternatively, the wide availability of reactive surface sites and layered structure of GO allows it to be a better candidate for developing free standing and GO/polymer hybrid membranes for water separation applications. GO nanosheets exhibit excellent antifouling capacity, a property greatly desired in the field of water desalination processes [19]. GO-based thin membranes exhibit promising qualities in the fields of a readily accessible, water permeable membrane to be incorporated in the desalination process [17]. GO films have also shown to be effective in allowing the flow of water while subsequently blocking penetration of other vapors, liquids, or gases [20].

This review highlights the preparation, characteristics and applications of functionalized NPG and graphene oxide (GO) membranes with the focus on their potential engineering into promising membrane materials for water desalination technologies. In the text, we refer to micropores and mesopores as "nanopores" for convenience because of their nanoscale pore widths. We will also cover the structural aspects of nano-channels across the graphene-based membranes and ion/molecule interaction with their sheets, the permeation and rejection mechanisms, and the mode of water transport in graphene nano-channels, as well as the latest advancement in graphene membrane fabrication and enhanced separation strategies. The emphasis will be on NPG and GO materials that participate directly in the desalination process or indirectly by providing selective properties such as anti-fouling, which could lead to next-generation desalination systems with increased efficiency and capacity.

2. Graphene structure and synthesis

Graphene can be defined as one-atom-thick 2D sheets, consisting of sp^2 bonded carbon atoms arranged in a hexagonal, honeycomb lattice. Due to their large theoretical specific surface area (2630 m^2 g^{-1}), high thermal conductivity (~5000 W m^{-1} K^{-1}), and excellent electrical conductivity, graphene has attracted a great deal of interest for over 40 years [21]. The most critical characteristic of graphene is its extremely versatile and tunable carbon backbone, leading to facile functionalization, and incorporation in a variety of applications [21]. The perfect one atom thick graphene sheets have been prominent for their impermeability to all standard gases [10,22,23]. Also, it can be fabricated on large scale as there is recent evidence of 30 inch multilayer graphene sheets being produced and transferred on roll-to-roll fabrication [24]. Stable defects in a graphene sheets, such as adatom vacancies, and topological defects were experimentally proven to be numerous and stable under electron irradiation. The electrical properties of graphene sheets can be altered by inducing defects through ion irradiation under ultra-high vacuum [25]. Defects induced in graphene trigger different charge