Desalination xxx (2015) xxx–xxx

Contents lists available at ScienceDirect

Desalination

journal homepage: www.elsevier.com/locate/desal

Nanoporous graphene as a reverse osmosis membrane: Recent insights from theory and simulation

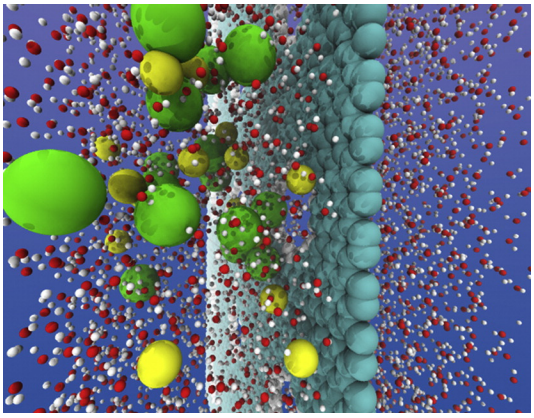
David Cohen-Tanugi, Jeffrey C. Grossman *

Department of Materials Science & Engineering, Massachusetts Institute of Technology, Cambridge, MA, USA

HIGHLIGHTS

- We review recent progress in the computational study of graphene as an RO membrane.
- We introduce graphene and current knowledge about its mass transport properties.
- We examine six key mechanisms that govern salt rejection in graphene.
- Molecular dynamics have played a dominant role in the study of graphene membranes.
- We suggest a greater role for quantum-level simulations and macroscale computation.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 23 November 2014
Received in revised form 30 December 2014
Accepted 31 December 2014
Available online xxxx

Keywords:
Graphene
Reverse osmosis
Simulation
Membrane technology
Molecular dynamics

ABSTRACT

In this review, we examine the potential and the challenges of designing an ultrathin reverse osmosis (RO) membrane from graphene, focusing on the role of computational methods in designing, understanding, and optimizing the relationship between atomic structure and RO performance. In recent years, graphene has emerged as a promising material for improving the performance of RO. Beginning at the atomic scale and extending to the RO plant scale, we review applications of computational research that have explored the structure, properties and potential performance of nanoporous graphene in the context of RO desalination.

1. Introduction

Desalination has seen important improvements in energy efficiency, reliability and economics since the 1960s thanks to numerous advances in reverse osmosis (RO) technology [1,2]. However, the semipermeable membranes that lie at the core of the RO process still rely on the same polyamide thin-film composite (TFC) design as three decades ago. As a result, the main improvements in RO membrane technology in recent decades (including the development of fully-crossed linked aromatic TFC membranes in the 1970s, of enhanced morphological control in the 1990s and more recently of nanostructured additives) have largely

* Corresponding author at: 77 Massachusetts Ave, Cambridge, MA 02139, USA.
E-mail address: jcg@mit.edu (J.C. Grossman).

http://dx.doi.org/10.1016/j.desal.2014.12.046
0011-9164/

been incremental rather than revolutionary. Thus, RO membranes leave tremendous room for improvement. The best TFC membranes today are only 1.5–2× more permeable than 20 years ago, and they still degrade in the presence of chlorine, making disinfection difficult and leaving them vulnerable to fouling [3]. In order for desalination to live up to the water challenges of the 21st century [4], a step-change is needed in RO membrane technology.

Graphene holds promise as an 'ultimate' RO membrane. It is stronger, thinner and more chemically robust than the polyamide active layers in TFC RO membranes, and researchers across disciplines have begun to explore this material's potential as a next-generation RO membrane [5–9]. At the same time, a number of physical and chemical phenomena involved in graphene-based desalination must be better understood in order to leverage the full potential of graphene for RO.

Thanks to significant advances in the field of computational materials science and simulation-based research in the past decades, it is becoming possible to answer some of the outstanding questions in the development of graphene-based RO membranes. Atomic-level simulations are helping to guide the development of functional graphene membranes in the laboratory through predictive materials design, and modeling techniques at the mesoscale and the macroscale are enabling a better understanding of the performance benefits and challenges that are likely to come in the development of graphene RO membranes.

In this review, we examine the role of computational methods in exploring the potential of graphene as an RO membrane. We begin with a brief introduction to graphene and its material properties, followed by an overview of the key computational methods that have been employed to date in the study of graphene for desalination. We then highlight work by our group and by others that has offered a computational proof-of-concept that nanoporous graphene could act as a water desalination membrane and that has explored the effect of graphene structure (in particular nanopore size and graphene chemistry) on RO performance. We then turn to the mechanical resilience of graphene and discuss the knowledge to date about the ability of graphene to withstand the hydraulic pressures required for RO without ripping. Finally, we discuss how computational methods can help predict the long-term economic and engineering benefits of graphene membranes at the plant-scale. While there are many reviews on graphene, and more recently reviews on the specific application of graphene and graphene oxide to mass separation [10] and desalination [11,12], in this paper we provide an in-depth look at the role of computational methods in developing single-layer graphene for RO.

2. What is graphene?

Graphene is a two-dimensional material that consists of a hexagonal (i.e., honeycomb) lattice of covalently bonded carbon atoms (see Fig. 1). Although it is the basic building block of graphite, and even though it had been studied since the mid-20th century [13,14], graphene has only been isolated in its freestanding, two-dimensional form in the past decade [15]. It has continued to fascinate researchers ever since, earning the researchers who pioneered its development a Nobel Prize in 2010 and becoming the subject of over 45 000 peer-reviewed research articles at the time of writing.

Much of the original interest in graphene arose out of the material's unique electronic properties, especially the fact that electric charge is carried throughout the material by so-called massless Dirac fermions [16] and that these Dirac fermions behave as a two-dimensional electron gas with ballistic transport behavior on the micrometer scale [17]. As a result of these properties, graphene is being investigated as a successor to silicon in mainstream electronics [18] and as a potential enabler of quantum computing [19], to name only a few examples.

However, it has come to light in recent years that graphene also holds significant promise for mass separation applications. In 2008, Bunch et al. demonstrated for the first time that pristine, defect-free monolayer graphene is impermeable to helium gas, and that the layer could form a membrane with a stiffness as high as ~1 TPa [20]. Jiang et al. subsequently added to the understanding of the promising mass separation behavior of graphene by predicting computationally that graphene with rectangular nanopores on the order of 0.34 nm could separate H_2 from CH_4 with a selectivity as high as 10^8, meaning that it is 10^8 times more permeable to H2 than to CH4 [21]. Meanwhile, it was also shown that nanoporous graphene (NPG) has potential for genetic sequencing applications by translocating individual DNA molecules through a nanopore [22–24]. The mass separation behavior of NPG suggests that it might also hold promise as an RO membrane for water desalination. In contrast with TFC membranes in which the precise mechanisms of salt rejection and water permeation are still not fully understood due to the amorphous nature of the polyamide active layer [3,25,26], the atomic thinness of graphene presents a more elegant and – in principle – simpler desalination process. However, the specific physical and chemical properties of ions in a hydrated environment and the complex hydrogen-bonding behavior of water at the nanoscale mean that NPG's ability to act as an effective RO membrane is far from obvious. Moreover, graphene remains a highly challenging material to characterize at the atomic scale experimentally. Therefore, computational methods, spanning from the atomic scale all the way to macroscopic modeling, are ideally suited to study these mechanisms and how they can be harnessed to design a radically new kind of RO membrane.

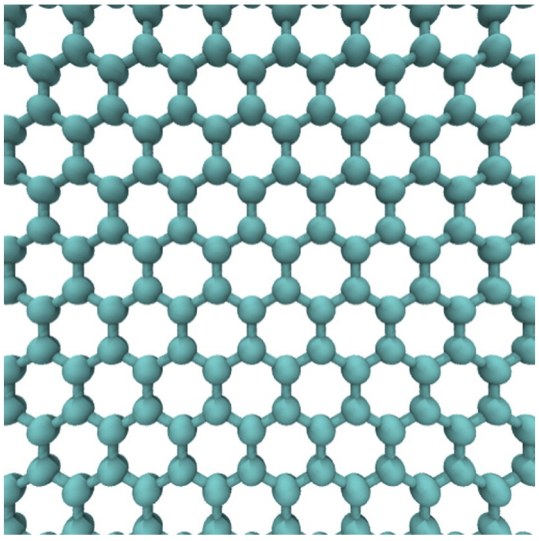


Fig. 1. Crystal lattice of graphene.

3. The role of computation

Computational materials science is rapidly becoming an essential component of research in energy technology, biomedical research, semiconductors and countless other fields. Ranging from macroscopic modeling all the way to atomistic simulations, computational methods have played an enabling role in the design and enhancement of solar cells [27–29], batteries [30,31], fuel cells [32], chemical sensors [33] and actuators [34,35], to cite only a few examples. Computational materials research can be employed to advance several types of objectives. Computation is especially helpful when the objective is *prediction*, e.g., for predicting a stable material structure or the relationship between material structure and properties. It is often successfully used for *understanding*, i.e., when the objective is to uncover the causal mechanism underlying a phenomenon, or to explain a surprising experimental observation. Finally, it can *provide guidelines* in the scientific process, e.g., by identifying the optimal regions of a material phase-space for a given application, or determining the most promising approaches towards experimentally making a material.

Please cite this article as: D. Cohen-Tanugi, J.C. Grossman, Nanoporous graphene as a reverse osmosis membrane: Recent insights from theory and simulation, Desalination (2015), http://dx.doi.org/10.1016/j.desal.2014.12.046