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A comprehensive review on wettability, desalination, and purification using graphene-based materials at water interfaces

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ABSTRACT

Graphene has several outstanding properties that make it suitable for use in a wide range of electronic devices and applications. Although the use of graphene has led to considerable increases in the performance of such devices, recent global concerns regarding water pollution have necessitated studies on graphene as a green material. The fact that graphene shows unique wetting characteristics and has a carbon-based porous structure suggests it should hold great promise for use in water desalination and purification. Thus, understanding the behavior of water at graphene interfaces is necessary for further enhancements in the desalination and purification processes. Hence, this review focuses on the recent advances made in these research areas, while considering the wettability of graphene, and aims to provide insights into the development of graphene-based water desalination and purification technologies.

1. Introduction

Graphene, a two-dimensional (2D) structured sheet consisting of sp^2-hybridized carbon atoms, has attracted great attention because it possesses outstanding mechanical, electrochemical, and thermal properties [1–4]. For example, ideal monolayered graphene has an ultrahigh specific surface area (2630 $m^2\,g^{-1}$) and shows an electron mobility of $2.5 \times 10^5\,cm^2\,V^{-1}\,S^{-1}$ and thermal conductivity of 5000 $W\,m\,K^{-1}$ [5]. Recently, with the development of methods for high-yield graphene production [6–9], there has been an exponential increase in the number of studies on graphene as an advanced material [10]. These studies have contributed to technological advances in various engineering fields. Thus, graphene research is expected to continue to increase in the future.

However, despite these developments, recent studies on graphene have mostly concentrated on its use in electronic devices and applications, such as high-speed electronics [11], data storage devices [12], displays [13], batteries [14], solar cells [15], and sensors [16]. Even though advancements in state-of-the-art electronics are essential for human development, graphene may be more useful to humans as an environmental material.

With concerns about water pollution growing all over the world in recent decades, finding new materials and technologies for water desalination (WD) and purification has become imperative. With the world population growing exponentially, the demand for drinking water has also increased dramatically. Thus, the issue of desalination has become an even more urgent one. Further, while these is a pressing need for advanced desalination technologies, the flow of hazardous wastewater from manufacturing and farming industries has become a threat to humans and the environment. This has increased the urgency of developing advanced purification technologies. Thus, economically feasible and scalable technologies for the desalination and purification of water need to be implemented not only for recycling water but also to protect humans from illnesses and the environment from the damage caused by the pollutants.

In this review, the potential of graphene-based materials for use in desalination and purification technologies is discussed, because such materials have extraordinary properties and can result in significant improvements in the desalination and purification of water.

2. Wettability of graphene

Because graphene is considered one of the most attractive coating materials discovered in recent decades [17–20], a deep understanding of its wettability properties is essential, in order to be able to use it in various applications, including in membranes [21,22], batteries

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[23–25], and cooling materials [26,27]. Accordingly, several recent studies have examined the effects of graphene wettability on its electronic and thermal performance. This has led to improvements in the energy-storage capacity and heat-transfer coefficient of the material [25,28]. Deep insights into the wettability of graphene will not only provide an understanding of the properties of graphene–liquid interfaces but should also result in improvements in the performance of graphene-based devices.

Depending on the range of water contact angles (WCAs) exhibited by a material, it can be classified as superhydrophilic, hydrophilic, hydrophobic, or superhydrophobic. The WCA of a hydrophilic surface ranges from 0 to 90°, whereas that of a hydrophobic surface ranges from 90 to 180° [29]. In particular, a surface with an extremely low WCA (~0°), which indicates a high surface energy, is considered superhydrophilic; conversely, a surface with an ultrahigh WCA (above 150°) is deemed superhydrophobic [30].

WCA measurements have been a popular method of evaluating the wettability properties of materials since Young introduced the following equation, which is called Young's equation [31]:

$$\gamma_{SG} - \gamma_{SL} - \gamma_{LG} \cos\theta = 0 \quad (1)$$

where θ is the contact angle (°) and γ_{SG}, γ_{SL}, and γ_{LG} are the surface energies of the solid–vapor, solid–liquid, and liquid–vapor interfaces, respectively (Fig. 1a). However, Young's equation is applicable only for perfectly flat and rigid surfaces, often called ideal surfaces; this limits its use in the case of actual surfaces, which are usually rough. To better elucidate the wettability of nonideal real surfaces as a function of the surface roughness, the Wenzel and Cassie–Baxter models can be used for homogeneous and heterogeneous surfaces, respectively [32,33]; these models are described by the equations given below. Note that homogeneous surfaces correspond to the case where water (or the liquid in question) adheres completely to the rough surface, and no trapped air is present (Fig. 1b). On the other hand, it is assumed that a considerable amount of air is trapped between the water (or liquid) and the textured surface in case of heterogeneous surfaces (Fig. 1c).

$$\cos\theta_{rough} = r \cos\theta_{flat} \quad (2)$$

where θ_{rough} and θ_{flat} are the WCAs of the rough and flat surfaces, respectively. Note that the θ_{flat} value is based on the assumption that the flat surface is composed of the same components as the rough surface. The roughness factor, r, is defined as the ratio of the actual surface area to the projected surface area; thus, the r value is always greater than 1. Accordingly, the Wenzel equation (Eq. (2)) suggests that increases in the roughness of hydrophilic ($0° < \theta_{flat} < 90°$) and hydrophobic ($90° < \theta_{flat} < 180°$) surfaces result in increased hydrophilicity and hydrophobicity, respectively.

$$\cos\theta_{rough} = f_1 \cos\theta_1 + f_2 \cos\theta_2 \quad (3)$$

In the Cassie–Baxter equation (Eq. (3)), f_1 and f_2 are the area fractions of the water and air phases, respectively, and θ_1 and θ_2 are the corresponding contact angles. Because air is trapped at the interface in the case of a heterogeneous surface, the contact angle of air is $\theta_2 = 180°$. Thus, Eq. (3) can be simplified as

$$\cos\theta_{rough} = f_1 \cos\theta_1 - f_2 \quad (4)$$

This indicates that θ_{rough} increases with an increase in f_2. That is to say, the microsized air bubbles attributable to the rough surface make the surface even more superhydrophobic. Hence, several studies on superhydrophobic surfaces have used the Cassie–Baxter model [34–38].

2.1. Intrinsic wettability of graphene

In contrast to the conventional belief that graphene is a hydrophobic material [39–42], it was recently claimed that graphene is hydrophilic and exhibits a low WCA (45°) [43–47]. According to these studies, the known hydrophobicity of the graphene is attributable to the inadvertent accumulation of hydrocarbons on its surface. Ashraf et al. [44] reported that early-stage WCA measurements of multilayered graphene indicate that it is hydrophilic whereas WCA measurements performed after exposures of 30 s, 1 min, and 1 day to the atmosphere showed that the WCA increases by up to 10°, 20°, and 40°, respectively, owing to the hydrocarbons present on the surface. Although the wettability of graphene remains a topic of debate because of these contradictory findings, the effect of airborne contaminants on the wettability transition seems quite clear [48–50]. For example, Arial et al. [50] showed experimentally that the WCA of graphene, which ranged initially from 61° to 85°, increased to 98° after prolonged exposure to air (Fig. 2). X-ray photoelectron spectroscopy (XPS) measurements revealed that airborne contaminants were adsorbed onto the graphene surface, resulting in a decrease in the surface energy by 10–16%.

However, it should be emphasized that most graphene samples that meet industrial standards show hydrophobicity [29,51–53]. This is because most fabrication methods that are economically viable and industrially scalable inevitably induce defects and wrinkles in the fabricated graphene, thus causing hydrocarbon contamination, which results in heterogeneous air-embedding graphene structures. For this reason, most studies on the applications of graphene have focused on its hydrophobic properties. In particular, the production of superhydrophobic graphene by structural and chemical modification techniques has attracted considerable attention with respect to specific applications, including self-cleaning, antifouling, and sensing [54–57]. Thus, in this review, we highlight some of the methods available for obtaining superhydrophobic graphene (see Section 2.3).

2.2. Wetting transparency of graphene

Before one can examine the superhydrophobicity of graphene, it is essential to elucidate one of its intrinsic properties. Rafiee et al. [28] reported that monolayered graphene deposited onto copper, gold, or silicon exhibits the wettability of the underlying metal substrate. This phenomenon of so-called "wetting transparency" is possible because of long-range van der Waals forces, which are active over distances of 5 nm (Fig. 3a). According to the wetting transparency theory, the other properties (i.e., electrical conductivity and thermal conductivity, among others) of the graphene-coated metal surfaces can be varied without changing their initial values. Similarly, Shih et al. [58,59] stated that monolayered graphene shows incomplete wetting transparency. For example, it exhibits wetting transparency on hydrophilic

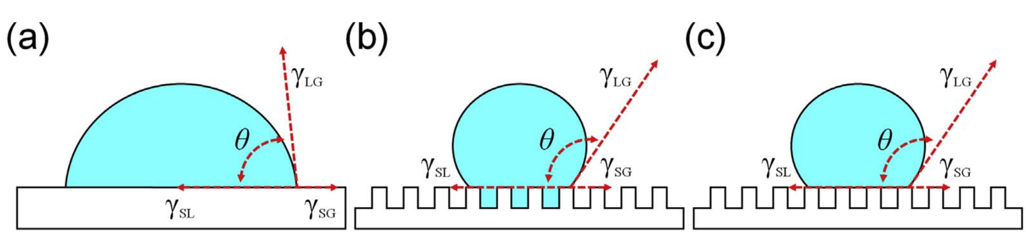

Fig. 1. Schematics of a water droplet on (a) flat and (b, c) rough surfaces, showing the balancing surface energies of Young's equation and the Wenzel and Cassie–Baxter models, respectively.