



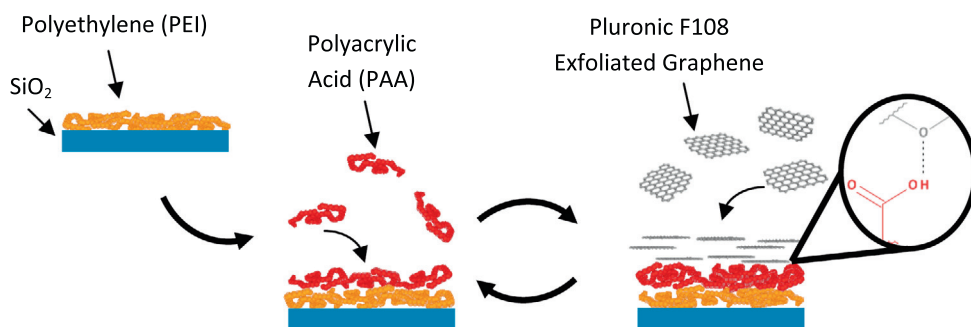
Graphene–polyelectrolyte multilayer film formation driven by hydrogen bonding



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GRAPHICAL ABSTRACT



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ABSTRACT

A method for preparing hydrogen bonded multilayer thin films comprised of layer pairs of surfactant stabilized graphene and an anionic polyelectrolyte is described. The films were constructed at low pH using the Layer-By-Layer (LbL) technique, where the adsorption of the cationic polyelectrolyte, polyethyleneimine (PEI) is followed by the sequential alternating adsorption of the anionic polyelectrolyte, polyacrylic acid (PAA) and anionic graphene sheets modified with Pluronic® F108, a polyethylene oxide–polypropylene oxide–polyethylene oxide (PEO–PPO–PEO) surfactant. Quartz Crystal Microbalance (QCM) measurements indicate that film formation was driven by hydrogen bonding between the carboxylic acid group of the PAA and ethylene oxide unit present in the surfactant. QCM measurements and Raman spectra showed evidence of non-linear and linear growth at low and high numbers of adsorbed layers respectively, suggesting overall superlinear film growth. Atomic Force Microscopy (AFM) Quantitative Nanomechanical Mapping (QNM) measurements of the films indicated that the reduced Young's Modulus of the films decreased with increasing numbers of adsorbed layers, reaching a bulk value of 6.07–32.3 MPa for samples with greater than 300 layers of surfactant stabilized graphene and PAA. The films were also shown to deteriorate partially with aqueous solutions at neutral and basic pH. The thin films exhibited features advantageous for use in coatings, such as pH responsiveness in addition to different mechanical properties, surface roughness, and internal structures based on the number of layers adsorbed.

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1. Introduction

Graphene, a single layer of sp^2 carbon atoms arranged in a hexagonal lattice, has attracted immense interest in recent years [1,2]. This is due in part to the superior electrical, mechanical and optical properties arising from its unique two dimensional structure. The remarkable properties of graphene also hold great potential for a myriad of functional applications, fuelling research efforts in a variety of areas including flexible electronics, photonics applications and functional coatings [3]. These potentially high-volume applications have necessitated the large scale production of graphene materials with two major technologies, graphene nanoplatelets and large area Chemical Vapor Deposition grown sheets currently dominating research efforts into graphene production.

Consequently, there are many methods of producing graphene nanoplatelets, one of which is the surfactant assisted ultrasonic exfoliation of graphite [4,5]. Unlike traditional mechanical exfoliation methods, ultrasonic exfoliation of graphite can be performed in aqueous conditions enabling large scale quantities of graphene particles to be processed. Ultrasonic graphite exfoliation also offers benefits over other liquid phase methods such as the Hummer's method, as it produces defect-free graphene sheets that retain their original planar structure [6,7]. Furthermore, the process is also facile, cost effective and non-hazardous.

The presence of surfactant species during the exfoliation process promotes the formation of high-concentration, aqueous graphene dispersions [7,8]. The addition of surfactant to a graphite suspension reduces the surface tension of the aqueous phase so that it matches the cohesive energy between graphene sheets, allowing exfoliation of the graphite to become energetically favorable. During this process, surfactant adsorbs to the surface of the graphene sheets, preventing reaggregation. A further increase in graphene concentration can be achieved by the continuous addition of surfactant, thereby maintaining the optimum surface tension throughout the sonication process [9].

One application where highly concentrated graphene dispersions are gaining increasing relevance is thin films and coatings [10,11]. Graphene is well suited for use in thin films due to its remarkable electrical conductivity, tensile strength and gas barrier properties. For example, thin conductive multilayer films containing graphene and polyelectrolytes have already been shown to act as effective oxygen barrier materials [12]. Electromagnetic shielding is another potential application for graphene based coatings. Consequently, the ability to incorporate graphene into thin films is an attractive research opportunity, providing the potential to create novel films for use in a range of applications such as food packaging, solar cells, and as a coating to supplement the existing gas barrier properties of thin polymer films.

The Layer-by-Layer (LbL) method is one possible route to constructing thin films embedded with graphene. The LbL technique is a simple, well established method of creating multilayer thin films on substrates from solution [13]. The resultant films possess a range of surface [14,15], mechanical [16] and electrical properties [17] that are influenced by the adsorbed species and are distinct from the underlying substrates [18,19]. Constructed LbL thin films also demonstrate the benefits of uniform surface coverage and highly controllable film thickness down to a few nanometers. As the technique can be performed independent of specialized equipment, it is well suited to a wide variety of fabrication processes including dip coating, spray coating and spin coating.

The LbL technique was traditionally used to fabricate multilayer thin films through electrostatic interactions, by sequentially adsorbing oppositely charged species, such as polyelectrolytes

onto a substrate [13,20–22]. However, it has also been shown that other non-electrostatic forces such as hydrogen bonding can also contribute to the successful construction of LbL multilayer films [23,24]. Compared to electrostatically assembled films, hydrogen bonded films offer a range of additional features such as pH [25] and temperature responsiveness [26], and cross linking at neutral pH [27].

Previous studies into the construction of LbL films using graphene dispersions have focused primarily on electrostatically assembled multilayer films [28,29]. For example, multilayer films have been constructed using the anionic polyelectrolyte polyacrylic acid (PAA) coupled with surfactant-exfoliated graphene modified with the cationic polyelectrolyte polyethyleneimine (PEI) [30]. More recently, multilayer films assembled from PEI and dispersions of low surface charge graphene particles, have also been formed [19]. The graphene particles were exfoliated and stabilized against reaggregation using the non-ionic surfactant Pluronic® F108. In this instance, the surfactant stabilized graphene particles were shown, using zeta potential measurements, to exhibit a small negative charge that decreased slightly with increasing pH. This charge arises due to the presence of oxygenated edge defects on the graphene sheets [30,31]. Consequently, the layers of polyelectrolyte and surfactant stabilized graphene were assembled through electrostatic forces. Together, these studies demonstrate the successful electrostatic LbL deposition of polyelectrolytes and surfactant stabilized graphene from the aqueous phase.

Conversely, few studies describe the assembly of weak polyelectrolytes and surfactant stabilized graphene dispersions into hydrogen bonded multilayer films. In one study, Gokhale et al. [12] used PEI coated graphene nanoparticles and PAA to form multilayer films via the LbL technique. Hydrogen bonding was encouraged by introducing each of the polyelectrolyte species into the multilayer at a pH below their respective pK_a . This ensured the carboxylic acid groups of the PAA and amine groups of the PEI existed in a largely uncharged state. However, these polyelectrolytes are known to produce electrostatically assembled multilayers in their charged states [32]. As a result, residual charges on the species may cause electrostatic interactions within localized regions of the hydrogen bonded multilayer film. These electrostatic interactions are not ideal as they limit the extra functionality that may arise due to hydrogen bonding [33].

As a result, this provides an opportunity to study systems which employ purely non-electrostatic interactions such as hydrogen bonding, in the fabrication of bulk LbL multilayer films from stabilized graphene and polyelectrolyte. Currently, the mechanical properties of hydrogen bonded multilayer films containing surfactant stabilized graphene and polyelectrolyte are also largely unknown.

In order to address these areas, this study presents a method of assembling thin films containing defect free, surfactant stabilized graphene particles, using hydrogen bonding. These films were prepared via the LbL approach, using the anionic polyelectrolyte PAA, and pristine graphene particles stabilized with a non-ionic tri-block copolymer (PEO-PPO-PEO) surfactant, Pluronic F108. Hydrogen bonding between the PEO portion of the surfactant and PAA is sufficient to produce stable multilayer films in the absence of electrostatic attraction between the anionic graphene particles, adsorbed non-ionic surfactant and anionic polyelectrolyte. Here, we propose a film growth pattern and internal film structure that is consistent with evidence from Quartz Crystal Microbalance measurements and Raman spectroscopic information. Interestingly, these films demonstrate an ability to be removed from surfaces using simple aqueous solutions, which may assist in controlled release applications.

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