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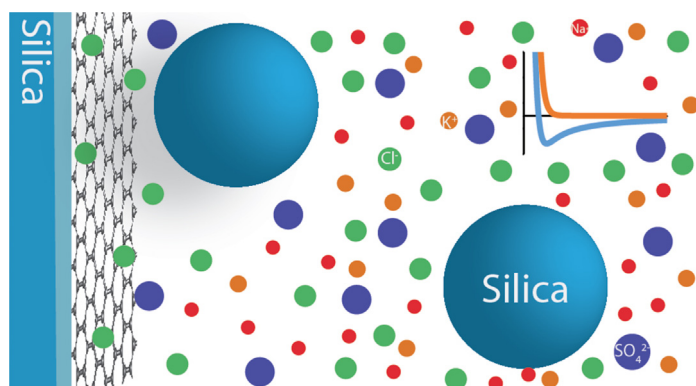
Evidence for negative charge near large area supported graphene in water: A study of silica microsphere interactions

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GRAPHICAL ABSTRACT

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ABSTRACT

This study addresses the electrostatic and van der Waals interactions at the aqueous interface of large area CVD graphene, 1–3 layers thick on a silica support and assessed by Raman spectroscopy to have exclusive sp2 character. Ionic strength was found to substantially alter the interactions of silica microspheres with silica-supported graphene. Particles were nonadhesive at large Debye lengths but became irreversibly adherent at reduced Debye lengths about 2 nm or less. This was demonstrated to be qualitatively parallel to the influence of ionic strength on silica-silica interactions. The observed ionic strength effects are best explained by negative charges in the vicinity, within a few nanometers, of the supported graphene. DLVO-based modeling of the silica-water-supported graphene interaction suggests that van der Waals interactions drive particle capture and that the surface potential at the supported graphene surface is at least -10 to -15 mV (corresponding to a charge density of 0.02–0.06/nm^2). This charge could result from ion adsorption or from charges on silica beneath the graphene. The conclusions are not substantially affected by inclusion of nanometer-scale interfacial roughness in the modeling.

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1. Introduction

Graphene is a two-dimensional material at the focus of intense research due to its unique electronic properties and varied applica-

tions in flexible electronics, biomaterials, and sensors [1]. The nature of the aqueous graphene interface is particularly important, not only because of its direct role in biomedical sensing[2–5], relevance to graphene toxicity, and physiological interactions [6–9], but also because graphene films with desirable optical and electronic properties may be created using surfactant-stabilized aqueous dispersions of exfoliated graphene [10–16]. It is therefore

important to understand the physical chemistry of the aqueous graphene interface, the factors responsible for the adsorption of polymers and surfactants, and the interactions responsible for adhesion of graphene to other particles, including cells and bacteria.

Different graphene-related materials are of general interest [11,17,18] (graphene oxide [11,18–20], reduced graphene oxide [11,21–23], and exfoliated graphite [17,24], epitaxial graphene on silicon carbide [25–27] and chemical vapor deposition [CVD] graphene film transferred to other substrates[28–30]), each having strengths for different applications. These different materials can have interactions dominated by different factors. For instance, graphene formed by CVD on copper and transferred to a support, while lacking the perfection of epitaxial graphene, is pure, continuous, and comprises an excellent means to cover large areas with sheets containing exclusive sp2 functionality (within detectible limits) and only modest local variations in layer number. By contrast, residual oxidation on reduced graphene oxide, or features at the edges of flakes can dominate some behaviors [11,22,23,31]. Aqueous inks of graphene flake are irregular and contain surfactants and other species, but may be formulated to retain desirable application-specific properties [16,31–33]. At the fundamental level, however, there are many remaining questions as to the physical chemical nature of the aqueous environment at the sp2 face of pristine graphene. The need to understand this base case (without deliberate oxidation and other chemistry) motivates the current study.

Compared with short-range highly-specific interactions such as pi-pi interactions, longer range forces potentially influence the interaction of graphene or supported graphene with approaching objects (as opposed to molecules). These interactions include hydrophobicity and van der Waals interactions. Water contact angle measurements, typically reflecting van der Waals forces and interfacial chemistry, were initially conflicting between various groups [34–36] but ultimately converged on a picture of single sheets of large area graphene as possessing intermediate (not super-) hydrophobicity [37–40]. Further, it was found that the water contact angle of supported single-layer graphene reflected contributions from the substrate [40,41]. Layer number-dependent contact angles were also thought to be a consequence of van der Waals interactions with the substrate. Not addressed, typically, are electrostatic interactions of graphene. In the case of pristine large-area graphene, perfect sp2 functionality eliminates the possibility of charge originating from surface groups such as carboxyls and alcohols. Other origins of graphene charge have not been addressed, with the exception of engineered holey graphene where the substrate may be accessible through the holes [42–44].

Interactions between suspended graphene micro-flakes (still only a few layers thick), for instance relevant to inks and dispersions are the focus of more recent studies [31,45–47]. Here, chemical functionality at the edge of flakes can contribute to interactions [11] and, while the hydrophobicity of the face of graphene flakes drives aggregation, it also facilitates surfactant adsorption [16,33]. The latter imparts dispersion stability through electrostatic or steric repulsion between flakes [31,45–47]. Kinetic measures of stability, compared with calculated interactions substantiate a DLVO approach at separations exceeding 1 nm for graphene oxide and surfactant-stabilized graphene flake [33,45,48–50]. By contrast, the interactions of colloid-scale objects with large area graphene, for instance in an aqueous environment, is an area less studied. Forces that are minimal at the molecular and nanoscopic levels, such as van der Waals interactions, scale differently and can be more significant for large objects. Also, the underlying support may influence graphene interactions as it does

for water contact angle, or through the formation of graphene wrinkles [51,52].

Building forward from studies of molecular interactions, contact angle, and exfoliated flake stability, this paper addresses the colloidal long-range interactions of silica-supported large area CVD graphene. These interactions are relevant both to particle and cell interactions and polymer and nanoparticle adsorption. Areas of single sheets are several millimeters on a side in our lab and up to centimeter scale in some other labs. In pH 7 buffer, the ionic strength is systematically varied and silica micro-particle capture on graphene is monitored and benchmarked against microparticle capture on the bare silica support. The microsphere capture rates, important in their own right in the context of sensing and assembly applications, provide insight into the microparticle pair potential with the supported graphene collector, following the same general mechanism by which colloidal aggregation kinetics reflect the particle pair potential [53]. Thus in addition to direct information about particle adhesion, new fundamental information about the supported graphene surface (charge, van der Waals interactions in water) is revealed, which will translate to the adsorption of other species. Worth mentioning, particle deposition/capture studies are powerful when based on well- defined and well-studied model materials such as those we employ, complimenting other methods such as streaming potential characterization of surface charge, or TIRM (total internal reflection microscopy) [54–56] and colloidal probe measures of the full interaction potential [57–59]. Indeed, the while the graphene employed here falls in the category of large area, it falls below that needed for standard streaming potential measurements on commercial instruments. Colloidal deposition with model particles is an alternative means to provide insight into the surface charge. Also, the colloidal deposition method we employ here accommodates a much wider range of ionic strengths (from 0 up to and exceeding 1 M) compared with streaming potential [60,61] or TIRM [55]. From colloidal deposition kinetics we can infer features of the interaction potential but the trade-off is that the potential itself is not directly measured.

We report here a surprising influence of ionic strength, with substantial repulsions at low ionic strength. The study includes an estimate of interactions based on DLVO calculations. The calculations, combined with the experimental observations, suggest that a low to moderate level of charge in the neighborhood of the graphene-water interface produces repulsion against negatively charged objects in solution and, that when salt is added, attractions from a secondary minimum are responsible for particle capture. Possible origins of the interfacial charge are discussed.

2. Results

2.1. Characterization

This work employed large area (7×7 mm^2) graphene sheets transferred, using a PMMA film as a support, to the surface of acid-etched microscope slides. The PMMA was subsequently dissolved in acetone and residual PMMA was removed by annealing at 240 °C. The Raman spectrum in the Supporting Information confirms the purity of the graphene (and lack of residual PMMA), in accord with the literature on pristine graphene [62], and suggests that the films are one, two, or three layers, in different regions of the surface. The XPS spectra in Fig. 1 additionally show that any residual PMMA is removed by the annealing step: Calibration spectra in the top part of the graph highlight features attributable to the PMMA while the lower spectra show the absence of these features after annealing.