Free Energy Relationships in the Electrical Double Layer over Single-Layer Graphene

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S *Supporting Information*

ABSTRACT: Fluid/solid interfaces containing single-layer graphene are important in the areas of chemistry, physics, biology, and materials science, yet this environment is difficult to access with experimental methods, especially under flow conditions and in a label-free manner. Herein, we demonstrate the use of second harmonic generation to quantify the interfacial free energy at the fused silica/single-layer graphene/water interface at pH 7 and under conditions of flowing aqueous electrolyte solutions ranging in NaCl concentrations from 10^{-4} to 10^{-1} M. Our analysis reveals that single-layer graphene reduces the interfacial free energy density of the fused silica/water interface by a factor of up to 7, which is substantial given that many interfacial processes, including those that are electrochemical in nature, are exponentially sensitive to interfacial free energy density.
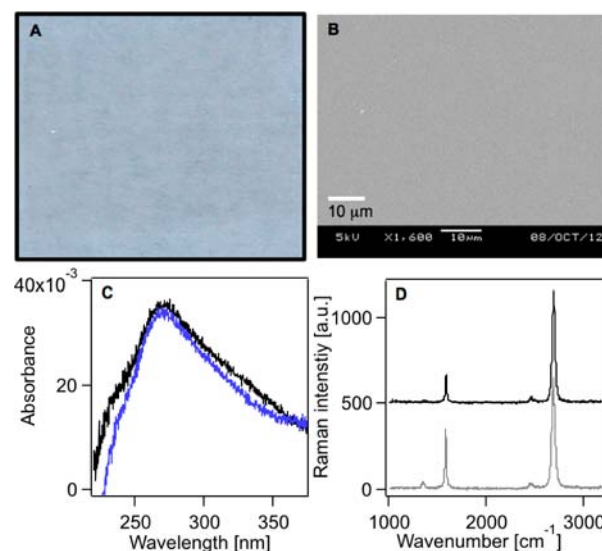
Figure 1. (A) Photograph and (B) scanning electron microscopy of the as-prepared graphene-deposited fused silica flats. (C) absorption spectra before (black trace) and after (blue trace) the SHG experiments. (D) Raman spectra of graphene single layers (top) and defect sites (bottom).

Graphene materials are important for a number of applications, including energy storage, catalysis, electronics, separations, and sensing.[1−7] While the relevant physical and chemical processes in energy applications usually occur at the fluid−solid interface, it is quite challenging to access this interface—and maybe even more importantly the electrical double layer above it—experimentally, without the use of labels and under aqueous flow conditions. Here, we overcome this challenge for the first time by applying second harmonic generation (SHG) to fused silica/graphene/water interfaces. We find a close to 7-fold reduction in interfacial free energy density when graphene single layers are placed between fused silica and water. This reduction of interfacial free energy density is reminiscent of charge screening and the resulting effective nuclear charge, Z_{eff}, by inner-shell electrons in an ion or atom. This result provides direct quantitative molecular-level information that can be used for understanding and predicting how aqueous-phase species interact with graphene localized at charged interfaces.

In the experiments, we prepare graphene single layers from chemical vapor deposition (CVD) of graphene grown on a copper catalyst and transferred onto a fused silica optical window following a previously reported procedure (see Supporting Information).[8] As shown in Figure 1 and the

Supporting Information, results from optical imagery, Raman spectromicroscopy, and scanning electron microscopy (SEM) are consistent[9−12] with the presence of millimeter-scale areas of single-layer graphene that have few holes. Furthermore, optical absorption spectra and contact angle measurements show that the graphene single layers do not wash off following exposure to aqueous electrolyte solutions under the conditions discussed here.

We recently applied sum frequency generation (SFG) in an orientational analysis of toluene on millimeter-thick samples of highly ordered pyrolytic graphite (HOPG). When tuned into the CH stretching region, the bare HOPG samples produced strong, nonresonant SFG signals on the order of 100 s of counts with 5-min-long signal integration times and a 500 fs time delay between the infrared and the visible up-converting

pulse.[13] In contrast to HOPG, the single-layer graphene sheets studied here produced weak SFG responses near 3 μm (i.e., 3000 cm^{-1}), requiring 20-min-long signal integration times even at zero time delay (Figure 2A). Similar to the observation
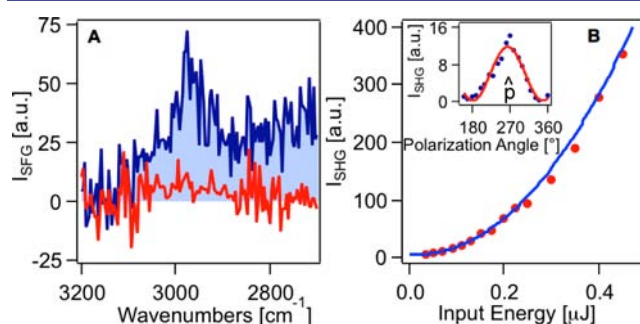

Figure 2. (A) ppp-Polarized SFG spectra of fused silica windows in air and in the presence (top) and absence (bottom) of single-layer graphene. (B) p-In/all-out-polarized SHG intensity at λ_{SHG} = 300 nm as a function of input pulse energy fit to a power function $y = a + bx^n$ (blue line), yielding $n = 2.1(1)$, and (inset) polarization dependence of the SHG intensity obtained using p-in-polarized fundamental light.

for graphene epitaxially grown on Ir(111) surfaces,[14] the nonresonant SFG response is devoid of sharp molecular features and simply reflects the bandwidth of the incident IR field. The SHG response of the fused silica/graphene/water interface is roughly 40 counts per second when probing with an input pulse energy well below the damage threshold of the system (0.15 μJ, Figure 2B). This SHG response is comparable in magnitude to that of the fused silica/water interface, which produces roughly 100 counts per second when probing with 0.3 μJ of visible light. As shown in Figure 2B, the SHG response from the fused silica/graphene/water interface is well polarized along the plane of incidence at λ_{SHG} = 300 nm when probing with p-polarized input light, which is in agreement with the results reported by Dean and van Driel,[15] and depends quadratically on input power.

Having established the damage threshold for studying single-layer graphene samples and staying well below it by working at 0.15 μJ of visible light, we applied the Eisenthal $\chi^{(3)}$ method[16,17] to determine the interfacial potentials and charge densities of the fused silica/water interface in the presence and absence of single-layer graphene at pH 7. The interfacial potential-dependent second harmonic electric field at 2ω, $E_{2\omega}$, is given by $\chi^3 E^2 \phi_0$, where χ^3 is the third-order susceptibility of the interface, E is the applied electric field at frequency ω, and ϕ_0 is the interfacial potential set up by the interfacial charges. These experiments were carried out on three different substrates for a minimum of two times each (see Supporting Information). We first collected the SHG response from each system in the presence of an aqueous phase adjusted to pH 7 by using small amounts of HCl and NaOH so as to keep the ionic strength between 1 and 10 mΩ and then added salt to the system.

Figure 3A shows that adding small amounts of salt to the system leads to a minor SHG increase, which is reminiscent of SFG intensity increases near 3400 cm^{-1} reported by Chou and co-workers for the OH stretches of interfacial water molecules for the same conditions.[18] We attribute this slight SHG signal increase at low salt concentrations to slight changes in the second- and third-order susceptibilities of the system as an electrical double layer is established at the interface, probably in the form of an inner and possibly outer Helmholtz layer. Once
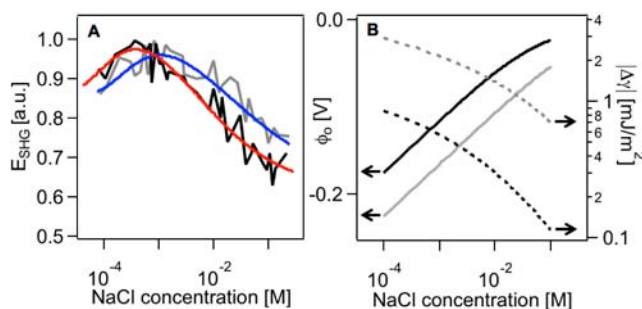

Figure 3. (A) p-In/all-out-polarized SHG response and (B) calculated interfacial potential (solid lines) and absolute free energy density (dashed lines) for the fused silica/water interface at λ_{SHG} = 300 nm as a function of electrolyte concentration at pH 7 in the presence (black) and absence (gray) of single-layer graphene, and fits (red and blue, respectively) of the Gouy−Chapman model modified by adding the equilibrium term necessary for describing the formation of the electrical double layer.

the salt concentration exceeds 1 mM, the SHG response decreases, which has been interpreted to screening of the interfacial charges as the diffuse layer builds up. The salt concentration at which the SHG response begins to decrease (1 mM) is the same that Hore and co-workers[19] and Chou and co-workers[18] reported for the onset of reductions in the SFG signal intensity of interfacial water molecules. It also coincides with the one for which Eftekhari-Bafrooei and Borguet reported the beginning of a substantial lengthening of the vibrational T_1 lifetimes for the OH stretching mode of water molecules within the fused silica/water interface, which was attributed to their incomplete solvation.[20,21]

Figure 3A clearly shows that the SHG response obtained from the fused silica/water interface decays faster with increasing salt concentration in the presence of graphene. Fitting the Gouy−Chapman model,[22] modified by adding the equilibrium term necessary for describing the formation of the electrical double layer (see Supporting Information), to the data yields an interfacial charge density of −0.013(6) C/m^2 for the fused silica/water interface, and an apparent attenuation of that charge density to 0.0049(8) C/m^2 in the presence of single-layer graphene. The same fit yields quite similar free energies for establishing the electrical double layer, namely 31(1) and 33.4(3) kJ/mol, at the fused silica/water interface in the absence and presence of graphene, respectively. Provided that the interfacial charge density of the fused silica/water interface is not altered in the presence of the graphene single layer, this result shows that a single-atom-thick layer of graphene can effectively screen the charges below it by more than 60%, while it has a negligible impact on the free energy associated with establishing the electrical double layer at room temperature and neutral pH. Alternatively, the result can be interpreted such that the presence of graphene reduces the interfacial charge density of fused silica by 60%. Either scenario yields the same important result for the interfacial free energy density in the diffuse layer that is shown in Figure 3B: here, the change in interfacial energy density, $\Delta\gamma$, is calculated using the Lippmann equation[22] according to $\Delta\gamma = -\sigma\Delta\Phi$, where σ is the interfacial charge density and $\Delta\Phi$ is the change in interfacial potential with changing electrolyte concentration calculated from the Gouy−Chapman model for the conditions of our experiment, referenced to zero potential. This analysis reveals that single-layer graphene reduces the interfacial free energy

density of the fused silica/water interface by a factor of up to 7, which is substantial given that many interfacial processes, including those that are electrochemical in nature, are exponentially sensitive to interfacial free energy density, or surface tension.[22]

We conclude that we have provided, for the first time, quantitative interface-specific thermodynamic information for understanding and predicting how aqueous-phase species can interact with liquid/solid interfaces in the presence of single-layer graphene. It is our expectation that these results will serve as important experimental benchmarks for theoretical calculations regarding the oxide/graphene/water system. Future work will focus on the adsorption of molecular and ionic solutes to interfaces decorated graphene sheets for studying a wide variety of interfacial processes relevant in energy science.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Information and data regarding CVD graphene sample preparation, SHG experimental setup and sample preparation, Raman analysis, contact angle measurements, and SFG experiments, including rotational anisotropy measurements, SHG E-field referencing and normalization procedure, and fitting. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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