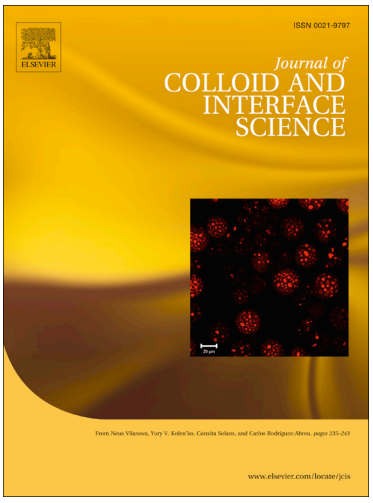

Tunable Fluorescence Quenching near the Graphene-Aqueous Interface

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Tunable Fluorescence Quenching near the Graphene-Aqueous Interface

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Abstract

With increased interest in graphene-based sensors for biomolecules and other targets, we investigated the impact of ionic strength on the steady-state emissions from fluorescein labels on proteins adsorbing on pristine CVD (chemical vapor deposited)-graphene on a silica support. Using the model system of fluorescein-tagged fibrinogen we demonstrated that, for fluorescein tags on adsorbed fibrinogen, emission intensity was very sensitive to the salt concentration. This behavior was not seen for fluorescein-tagged fibrinogen in solution. We demonstrated that fluorescein "quenching" in this system was a result of fluorescein's pH sensitivity: with changes in salt concentration, near-surface fluorescein experiences either the neutral bulk pH or, with a negatively charged surface, an acidic environment. The findings carry the important implication that the aqueous environment near silica-supported graphene is substantially acidic as a result of near surface negative charge. This further implies, because of the purity of the graphene in this study and its lack of oxidation, that negative charge arises from ion adsorption and/or from the underlying silica support, which may be hydrated and present dissociated surface silanols. That is, the electrostatic potential from silica beneath the graphene may pass through the graphene, much as van der Waals interactions have been proven to do. Results were semi-quantitatively consistent with calculations that employed a Guoy Chapman model of the interface and the established pKa of the fluorescein. While these findings were obtained with adsorbed proteins, similar fluorescence quenching would be expected for any fluorescein-tagged species in the vicinity of silica-supported graphene. Thus, because of the negative charge at the aqueous graphene interface, ionic strength can be exploited as means of creating a molecular ruler of fluorescein emissions, and the emissions can be assessed within different distances, corresponding to the Debye length, from the graphene interface.

Keywords: graphene, protein adsorption, fluorescence quenching, biosensor