

Charge and Molecular Transport at Large Area, Single Layer Graphene Electrodes

Nicole L. Ritzert, Joaquín Rodríguez-López, Cen Tan,
Jason A. Mann, William R. Dichtel,
and Héctor D. Abruña

Department of Chemistry and Chemical Biology
Cornell University
Ithaca, NY 14853

Abstract

Graphene, a one-atom thick layer of sp^2 carbon, has demonstrated interesting physical and electronic properties.¹ Its well-defined geometry, flexibility, and high transparency make it an attractive platform for producing highly reproducible contacts to molecules in devices such as photovoltaics, flexible electronics, sensors, and field-effect transistors.² Therefore, it is of great interest to understand charge and molecular transport at graphene surfaces.

We used scanning electrochemical microscopy (SECM) to probe the heterogeneous electron transfer kinetics of several electron transfer mediators at chemically vapor deposited (CVD) single layer graphene electrodes.³ SECM provides the ability to measure electron transfer kinetics while minimizing effects from resistance. Some mediators in aqueous media, such as hexacyanoferrate (II/III) and iron (II/III) ethylenediaminetetraacetic acid, exhibited quasi-reversible electron transfer at bare graphene whereas the kinetics of others, including methyl viologen and hexaammine ruthenium (II/III), was nearly reversible.

We generated a library of mediators that we can use to probe the effects of deliberate modifications to graphene. For quasi-reversible mediators, electron transfer at graphene was enhanced in the presence of a fraction of a monolayer of an adsorbed osmium complex, demonstrating the effect of defects on the observed electrochemical behavior of graphene. This enhancement provided a contrast between the more active, modified graphene and the less active, bare graphene surface. We used this difference in kinetics to probe tripodal molecules containing an electroactive cobalt group and aromatic feet designed to adsorb to the graphene surface.⁴ By using the SECM to image areas of adsorbed tripod molecules over time, we determined their surface diffusion coefficient.

Currently, we are investigating other ways of using non-covalent modifications to control the charge transfer properties of single layer graphene.

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