Probing Structure Function Relationships with Graphene Monolayer Electrodes: The Importance of Disorder for Enhanced Electrochemical Performance

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Abstract

Graphene-based electrodes hold promise for a wide variety of electrochemical applications such as in supercapacitors, electrochemical sensors and as electrocatalysts. While fundamental electrochemical studies have been carried out on mechanically exfoliated (Scotch-tape) graphene and vapor deposited materials, most applications require thicker, porous electrodes assembled from aggregated submicron-sized graphene typically obtained by thermal or chemical reduction of graphene oxide. In general, the porous nature of the resulting films precludes a quantitative analysis of, for example, interfacial capacitance or rates of important electrochemical reactions.

In this talk, we present a general method for characterizing the intrinsic electrochemical properties of graphene sheets in the absence of porosity-related artifacts and uncertainties.[1] This is achieved by assembling graphene monolayers at the air-water interface and transferring films with controlled packing density to various electrode substrates. This system allows us to characterize various graphene-based materials in a well-defined 2D geometry and provides the most effective means of holding morphology and surface area constant while investigating the effects of inherent or intentional structural and chemical changes to these materials. [2 - 5]

Using this model system we demonstrate the enormous changes in intrinsic electrochemical properties that are observed as the level of defects and functionalities are varied through various thermal and chemical treatments. Under optimal annealing conditions a four-fold increase in the intrinsic capacitance of the graphene/electrolyte interface is observed indicating that the graphene production or post-treatment method can have a significant impact on the theoretically achievable capacitance and energy density of high voltage, graphene-based supercapacitors.[3] Furthermore, we demonstrate changes in reaction rate constants by over two orders of magnitude for electrocatalytic applications such as the oxidation of NO [4] or the redox activity of the Co(byy)3(II/III) mediator used in dye sensitized solar cells. In all cases, performance improvements were observed for functionalized graphene which exhibit a significantly disordered structure emphasizing that, for many applications, the residual defects and functional groups on reduced graphene oxide are more beneficial than the more ordered structure of pristine graphene.

References

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