

Insights into Physicochemical Interfacial Processes and Electroactive Site Density Distribution using Scanning Electrochemical Microscopy for Graphene-based Hybrids

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Surface (and interfacial) science is found in various environments of scientific significance including biomembranes, ocean and atmospheric chemistry, applied electrochemistry and at the grand challenges of *energy-water nexus* [1]. Molecular redox behavior on the surface and at the interface is drastically different than bulk counterparts.

In this talk, we demonstrate scanning electrochemical microscopy (SECM) is a powerful tool to investigate dynamic physical-chemical processes at surfaces and buried interfaces. This technique helps to determine ion (or electron) transfer kinetic rate, diffusion coefficient, imaging electrochemical redox reactions and activity. The significant advantage offered by SECM is its capability of probing chemical information at the solid/liquid interfaces. A constant potential is applied to the tip and electrochemical working electrode (*i.e.* the substrate in electrolyte) to drive reaction of redox species (or mediator) in bulk electrolyte solution to probe the surfaces of graphene-based hybrids, relevant for electrochemical energy systems. The micro-configured cyclic voltammograms, probe approach curves in feedback and imaging modes, for graphene/CNT, graphene/transition metal oxide and aerogels are chosen as case examples to probe ion adsorption, charge transfer dynamics and to map highly electroactive ('hot spots') edge sites. The SECM setup has a resolution of ~40 nm and can locate and relocate areas of interest precisely after a coarse image. The heterogeneous electrode surfaces comprised of graphene nanosheets (conducting)/other nanomaterials (semiconducting) exhibit peak and valley tip current behavior and site distribution and the data is analyzed in terms of reactive basal plane and edge plane sites distribution, and help to determine heterogeneous rate constant using modeling and fitting experimental data. The findings reinforce the available electron density of states in the vicinity of the Fermi level contributing to higher electroactivity, faster interfacial diffusion, and shorter distances for electron transfer, facilitated through molecular and chemical bridges [1].

[1] S. Gupta and S. B. Carrizosa, Appl. Phys. Lett. **109**, 243903 (2016).

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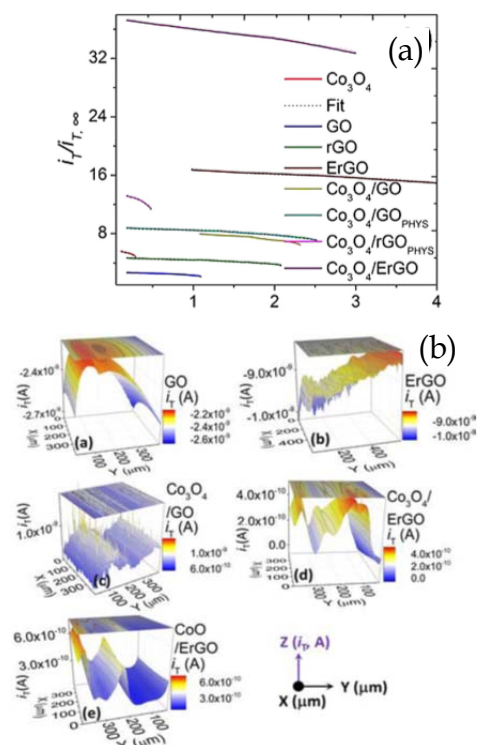


Figure 1. (a) Probe approach curves at solid/liquid interface with redox mediator $10\mu\text{M}$ FcMeOH in base electrolyte 0.5M KOH with $V_t = -0.5\text{V}$ and $V_s = -0.4\text{V}$. The corresponding theoretical fitting is plotted as dash curves. (b) Representative SECM images displaying current distribution with the occasional higher (peak)/lower (valley) current behavior. A color bar is shown for quantitative values of the tip current [1].