

Spectroelectrochemical Investigations of Electrochemical Processes using Carbon Optically Transparent Electrodes

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This presentation will present several case examples using carbon optically transparent electrodes (C-OTEs) as a stable and efficient spectroelectrochemical platform for detailed study of electrochemical processes and interfaces. While C-OTEs have been utilized in a limited context as electrodes for spectroelectrochemistry and fluorescence imaging applications, their method of preparation has limited practical application as optically transparent electrodes. Yet C-OTEs generated through pyrolysis of diluted photoresist, a method pioneered by McCreery, produces pyrolyzed photoresist films (PPFs) of reproducible nature with interesting physicochemical properties. In this presentation, we will present several case examples of C-OTEs as improved platforms for studying electrochemical systems. For instance, we have utilized these electrodes for oxidative-reductive electrogenerated chemiluminescence (ECL) that display a low oxidation potential for co-reactant ECL as the hydrophobic electrode surface facilitates adsorption of co-reactants to generate intense ECL.¹ Furthermore, the PPF generated C-OTEs exhibit wide electrochemical windows of stability and high degree of optical transparency in the UV region (> 35% transmittance over 190-400 nm, and 45-61% for 400-1000 nm for the thinnest C-OTEs of 11-nm thickness). The C-OTEs perform favorably versus ITO in both oxidative-reductive and reductive-oxidative ECL studies, and are observed to be much more stable in both acidic and alkaline solutions. In another case example, we will demonstrate how C-OTEs can be used to study the formation of electrogenerated graphitic oxides (EGO) using a combined UV-Vis spectroelectrochemical approach.² Monitoring of the π - π^* aromatic carbon transition for reduced graphene oxide (rGO) at 270 nm and graphene oxide at 230 nm, we can follow the growth of GO in KCl upon applying oxidizing potentials. X-ray photoelectron spectroscopy (XPS) and time of flight secondary ion mass spectroscopy (TOF-SIMS) are used to confirm sample composition and location of salt ions within the electrode. Formation of EGO is stable enough to be observed by UV-Vis and new mechanism is established that is unique to alkali chloride supporting electrolytes due to formation of a solid-electrolyte interphase (SEI) which incorporates the alkali cation to stabilize the negatively charged oxygen functional groups while the presence of chloride anion acts as a passivation agent that protects the electrode surface from dissolution. This spectroelectrochemical approach highlights the detection and study of electrochemical processes that cannot be detected by electrochemical measurements (i.e. I-V plots) alone.

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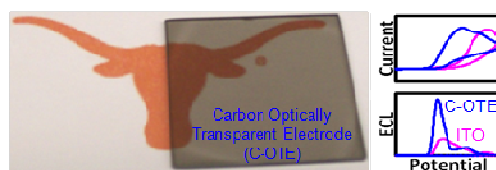


Figure 1. Carbon optically transparent electrodes prepared by pyrolysis of photoresist enabling high resolution study of electrochemical processes and interfaces.

References.

1. Walker, E. K.; Vanden Bout, D. A.; Stevenson, K. J. "Carbon Optically Transparent Electrodes for Electrogenerated Chemiluminescence," *Langmuir* **2012**, 28(2), 1604-1610.
2. Walker, E. K.; Vanden Bout, D. A.; Stevenson, K. J. "Spectroelectrochemical Investigation of an Electrogenerated Graphitic Oxide Solid Electrolyte Interphase," *Anal. Chem.* **2012**, 84(19), 8190-8197.