

Electrochemical Characterization of Carbon Films with Highly Porous Microstructures

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CANADA

Carbon is widely used as an electrode material for analysis and as a substrate for modified electrodes mainly because of its wide potential range, solvent compatibility and relatively low cost. Electrochemical performance of numerous forms of carbon materials such as glassy carbon (GC) [1], carbon fibers [2], photoresist derived carbon films [3] and highly ordered pyrolytic graphite (HOPG) [1] have been reported. Results from these studies show that the carbon surfaces differ significantly in electrode transfer reactivity. Hence, the suitability of the electrode material for electroanalysis varies among the various forms of carbon. In this study, the electrochemical performance of carbon films formed via a recently developed film fabrication technique called glancing angle deposition (GLAD) is investigated.[4] The GLAD technique involves vapor deposition of thin films onto unheated substrates oriented at highly oblique angles to the vapor flux. Two competing mechanisms namely, self-shadowing and limited adatom diffusion dominate the growth process.[4] The porosity of GLAD films arises from the self-shadowing effect and increases as the angle between the substrate normal and the incident vapor is made increasingly oblique. The shape of the micro-columns can be tailored by varying the substrate rotation rate. GLAD technique is employed here to fabricate carbon films with helical microstructures (Figure 1) onto a silicon substrate. The GLAD carbon films have controllable porosity and microstructure on the 10-nanometer scale. The fabricated carbon films were characterized by scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). In addition, several electrochemical characterizations commonly used to probe the reactivity of carbon electrodes were applied to the fabricated carbon films. The GLAD carbon films were compared to polished GC and graphite electrodes in order to determine their electroanalytical performance. The cyclic voltammetric peak separation (ΔE_p), for several redox systems were utilized to assess the electron transfer reactivity on the carbon films. The redox systems employed were selected based on their known kinetic behavior on carbon surfaces. For example, heterogeneous electron transfer kinetics for $\text{Fe}(\text{CN})_6^{3-/4-}$ is known to be sensitive to surface cleanliness and active sites. For this system, the GLAD carbon film surfaces show slightly slower electron transfer kinetics than GC but faster kinetics than graphite. This suggests that the fabricated GLAD carbon films likely have a more active surface than graphite (which is the vapor source) but results in a less active surface than GC. We have also employed aquated $\text{Fe}^{3+/2+}$ redox couple as a probe to the surface structure of the carbon films. This redox system is well known to be very sensitive to presence of surface oxides, especially surface carbonyl groups. The ΔE_p value measured on the GLAD carbon films is found to be very large signifying a slow electron transfer reaction. The weak interaction between the GLAD carbon film and the $\text{Fe}^{3+/2+}$ redox system lead to the slow kinetics. This is caused by the low density of surface oxides at the surface of the fabricated carbon films as confirmed by the XPS studies. The GLAD carbon films exhibit a high

background current as compared to GC or graphite electrodes. The high background current may be attributed mainly to the large surface area and porosity of the carbon films. The ΔE_p values measured on the GLAD carbon films are reproducible with a standard deviation less than 10 %. We have also chemically modified the GLAD carbon films and investigated their electrocatalytic behavior towards biological and analytical applications. The modified carbon films show favorable catalytic activity with $\text{Fe}^{3+/2+}$ redox system and biological molecules such as dopamine. The background current increases following chemical modification likely due to increase in surface charge. Overall, the GLAD carbon films show very stable electrochemical behavior.

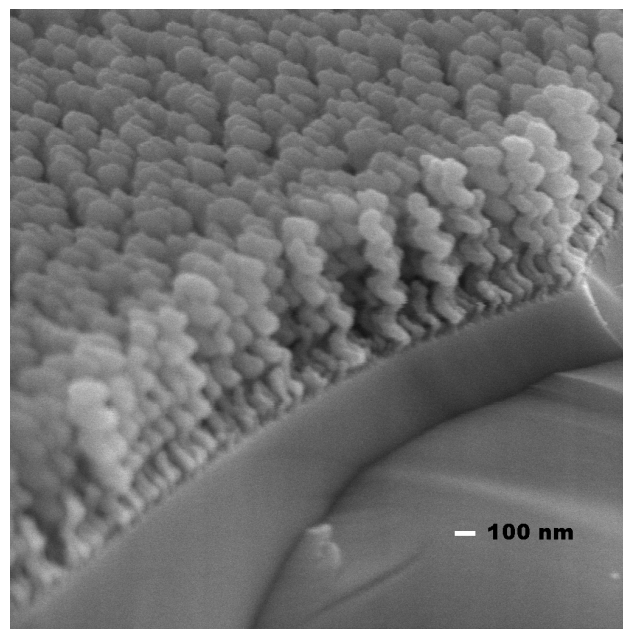


Figure 1. Scanning electron micrograph image of GLAD carbon film deposited onto silicon substrate showing a helical microstructure.

References

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