

Direct Electrochemistry of Glucose Oxidase at a Gold Electrode Modified with Single-Wall Carbon Nanotubes

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Abstract: The direct electrochemistry of glucose oxidase (GOD) was accomplished at a gold electrode modified with single-wall carbon nanotubes (SWNTs). A pair of well-defined redox peaks was obtained for GOD with the reduction peak potential at -0.465 V and a peak potential separation of 23 mV at pH 7.0. Both FT-IR spectra and the dependence of the reduction peak current on the scan rate revealed that GOD adsorbed onto the SWNT surfaces. The redox wave corresponds to the redox center of the flavin adenine dinucleotide (FAD) of the GOD adsorbate. The electron transfer rate of GOD redox reaction was greatly enhanced at the SWNT-modified electrode. The peak potential was shown to be pH dependent. Verified by spectral methods, the specific enzyme activity of GOD adsorbates at the SWNTs appears to be retained.

Keywords: Glucose oxidase ; SWNT-modified electrode; Direct Electrochemistry

Introduction

Carbon nanotubes (CNTs) possess superb electrical conductivity, high chemical stability, and extremely remarkable mechanical strength and modulus [1]. These tubes can be divided into two categories. Multiwall carbon nanotubes (MWNTs) and single wall carbon nanotubes (SWNTs).

MWNTs are made of concentric cylinders placed around a common central hollow, with an interlayer distance close to that of graphite (0.34 nm). Single-wall carbon nanotubes (SWNTs) are usually arranged in a regular pattern of bundles composed of tens to hundreds of carbon nanotubes in parallel and in contact with each other. CNTs have been shown to be advantageous for a wide range of potential and practical applications, such as electronic devices [2], probe for scanning probe microscopy [3], high sensitivity nanobalance for nanoscopic particles [4] and chemical sensors [5,6]. Recent developments in carbon nanotubes have been reviewed [1,7].

Depending on its atomic structure, carbon nanotubes behave electrically either as metals or as semiconductors [8,9]. The subtle electronic properties suggest that carbon nanotubes have the ability to promote electron transfer reactions when used as an electrode material in electrochemical reactions. The application of CNTs in electroanalytical chemistry has been receiving more and more attention [10-26]. Carbon nanotubes can serve as excellent substrates for the development of biosensors or as a modifier to promote electron transfer reactions between many biologically important species with the underlying electrode. The immobilization of protein and enzyme onto CNTs is leading to the development of new biosensors [27-29].

Study of the direct heterogeneous electron transfer of proteins and enzymes is a convenient and informative means for understanding the kinetics and thermodynamics of biological redox processes [30]. The direct electrochemistry of the flavoenzymes has been widely investigated. However, in the absence of mediating small molecules, well-defined direct electrochemical behavior of flavoprotein-oxidase systems is rendered extremely difficult as the flavin adenine dinucleotide (FAD) moiety is deeply embedded within a protective protein shell. Glucose oxidase is a typical flavin enzyme with FAD as redox prosthetic group. Its biological function is to catalyze glucose to form gluconolactone. The GOD molecule is a structurally rigid glycoprotein with a molecular weight of 152,000-186,000 Da, and consists of two identical polypeptide chains, each containing a FAD redox center. However, in general the GOD is not oxidized electrochemically through the electrode reaction. The reason is that the FAD/FADH₂ redox centers are located deeply in the apoenzyme [31]. Recently, a great number of methods have been developed to achieve direct electron transfer between the GOD and various chemically modified electrodes [32-34].

In present, novel carbon materials are evaluated as transducers, stabilizers and mediators for the construction of amperometric biosensors [35]. It is shown that carbon nanotubes are promising materials as electrochemical mediators and enzyme stabilizers. Based on the consideration that carbon nanotubes might be the best candidate among the various carbonaceous substrates for promoting the electron transfer reaction of GOD and for biomolecular attachment [29,36], we explored the possibility of direct chemistry studies of GOD at SWNT-modified gold electrodes. We now wish to report the preparation of SWNT-modified gold electrodes for the studies of direct electrochemistry of GOD. The analytical performance of the SWNT-modified electrodes is described and a spectroscopic evidence is presented to show the retention of the specific enzyme activity of GOD at the SWNT-modified surfaces. Our work demonstrates that carbon nanotubes might be a unique material for the fabrication of useful biosensors.

Experimental

Reagents and Instruments

Purified SWNTs were purchased from SES Research (Houston, TX). All solutions were prepared with deionized water treated with a Millipore water purification system (Millipore Corp.). Glucose Oxidase was acquired from Sigma and dissolved in a phosphate buffer solution (0.05 M, pH 7.0).

Voltammetric measurements were performed with a CHI 660 electrochemical workstation (CH Instruments, Austin, TX) in a conventional three-electrode cell. The working electrode was a Au disk electrode with a diameter of 2 mm. Prior to each measurement, the electrode was polished with diamond pastes and an alumina slurry down to 0.05 μm on a polishing cloth, followed by sonicating in water and ethanol. The electrode was rinsed with a copious amount of deionized water. A saturated calomel electrode (SCE) and a platinum electrode were used as the reference and auxiliary electrodes, respectively. Unless otherwise stated, the electrolyte solutions were thoroughly degassed with N_2 and kept under a N_2 blanket.

FT-IR spectra were collected using an Avatar 360 FT-IR spectrometer (Nicolet Instrument Corp., Madison, WI).

Preparation of GOD/SWNTs Modified Electrode

With the aid of ultrasonic agitation, 1 mg of purified SWNTs was dispersed in 10 mL of N,N-dimethylformamide (DMF). To modify the gold electrode with SWNTs, 15 μL of the SWNT suspension was cast onto the gold electrode and the solvent was allowed to dry under an infrared lamp. The preparative procedure was found to produce optimal voltammetric responses. Too little of the casting solution will not yield discernible voltammetric currents, whereas too much will increase the background current so much that the redox peaks became distorted. The resulting electrodes were sequentially rinsed with water and the working buffer just before carrying out CV experiment. In order to prepare GOD/SWNTs modified electrode, 5 μL $1.0 \times 10^{-4}\text{M}$ GOD solution was dropped onto the surface of the SWNTs modified electrode then allowed to dry under ambient conditions. Also, GOD/SWNTs electrodes were rinsed completely with water and the working buffer solution prior to carry out CV experiment.

To measure the FT-IR spectra, silicon (100) wafers were used as the substrate for supporting the SWNT films (prepared in a similar manner to that for the Au disk electrode except that SWNT was dispersed in ethanol).

Results and Discussion

Direct electrochemistry of GOD at the SWNT-modified Au electrode

Cyclic voltammograms (CVs) overlaid in Figure 1 show the redox behaviors of GOD in a 0.05 M phosphate buffer solution (pH 7.0) at a bare gold electrode (curve 1) and at a

GOD/SWNT-modified Au electrode (curve 3). The CV acquired at the SWNT-modified gold electrode in the absence of GOD (curve 2) is also given. As can be seen, while GOD at a bare gold electrode essentially exhibits no voltammetric response, a pair of well-defined redox peaks was observed at the GOD/SWNT-modified electrode. The absence of any discernable faradaic current in curve 2 suggests that the observed peaks in curve 3 is not given rise by the SWNTs. For curve 3, at pH 7.0 and ν (scan rate) of 0.1 Vs^{-1} , the cathodic peak potential (E_{pc}) is -0.465 V vs. SCE and the peak potential separation (ΔE_p) is 23 mV . The ratio of the cathodic current over the anodic one is close to 1, suggesting that GOD undergoes a quasi-reversible redox process at the SWNT-modified electrode. The peak potential and the voltammetric characteristics are consistent with reported values for free FAD and the FAD redox center of the flavoenzyme[31,37]. The large background current is attributable to the catalytically active surface of the modified electrode. SWNTs, with diameters in the range of 1-2 nm, and up to several microns in length, have very high aspect ratio (length versus diameter). When used as an electrode material, the surface area of the electrode is increased. Consequently, the background current at the SWNT-coated surface is greater than that at the bare surface.

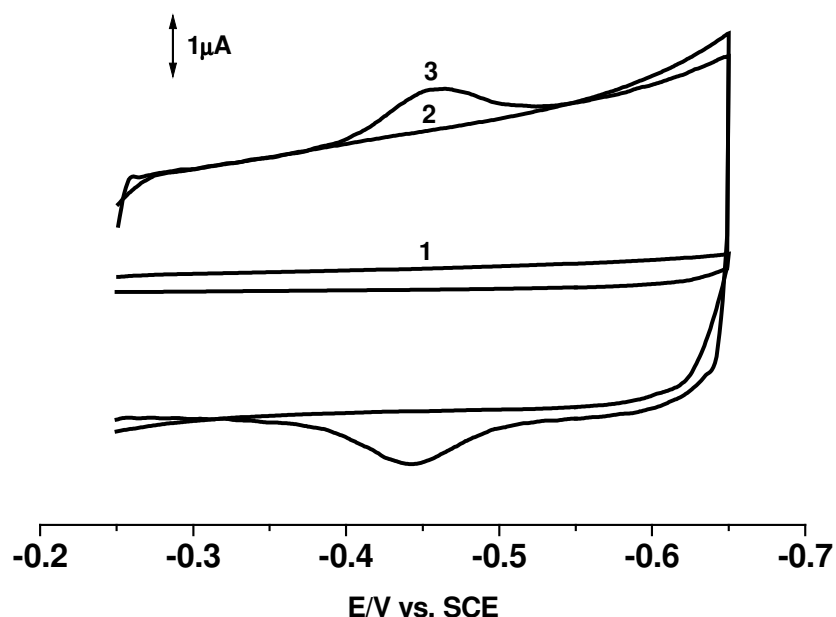


Fig.1. Cyclic voltammograms of glucose oxidase ($1.0 \times 10^{-4} \text{ M}$) at a bare gold electrode (1) and a SWNT-modified gold electrode (3). Curve (2) is a voltammogram acquired at a SWNT-modified gold electrode in the absence of glucose oxidase. The electrolyte solution used was a 0.05M phosphate buffer (pH 7.0) and the scan rate employed was 0.1 Vs^{-1} .

A voltammograms at unmodified glassy carbon electrodes and found that the voltammetric response (data not shown) was comparable to curve 1. Thus, it is conclusive that SWNT-modified surface indeed enhances the electron transfer rate.

Effect of Scan Rate on the Peak Current and Peak Potential of GOD at an SWNT Film-Modified Electrode

The influence of the scan rate on the electrochemistry of GOD at the SWNT film modified electrode was investigated by cyclic voltammetry. Figure 2 displays an overlap of CVs of GOD acquired at five different scan rates. The i_{pc} - v plot shown in the inset exhibits a linear relationship (with $r = 0.9991$). Moreover, ΔE_p remains virtually constant within the range of scan rates studied. Thus, it is clear that GOD adsorbed onto the surface undergoes a reversible electron transfer with the SWNTs. The reason for the facile electron transfer reaction is that the surface of SWNTs are known to enhance many electrochemical reactions [13,38,39]. The better performance of the carbon nanotube electrodes has been found due to the carbon nanotube dimensions (of the tubes, the channels that are inherently present in the tubes), the electronic structure, and the topological defects present on the tube surface [39].

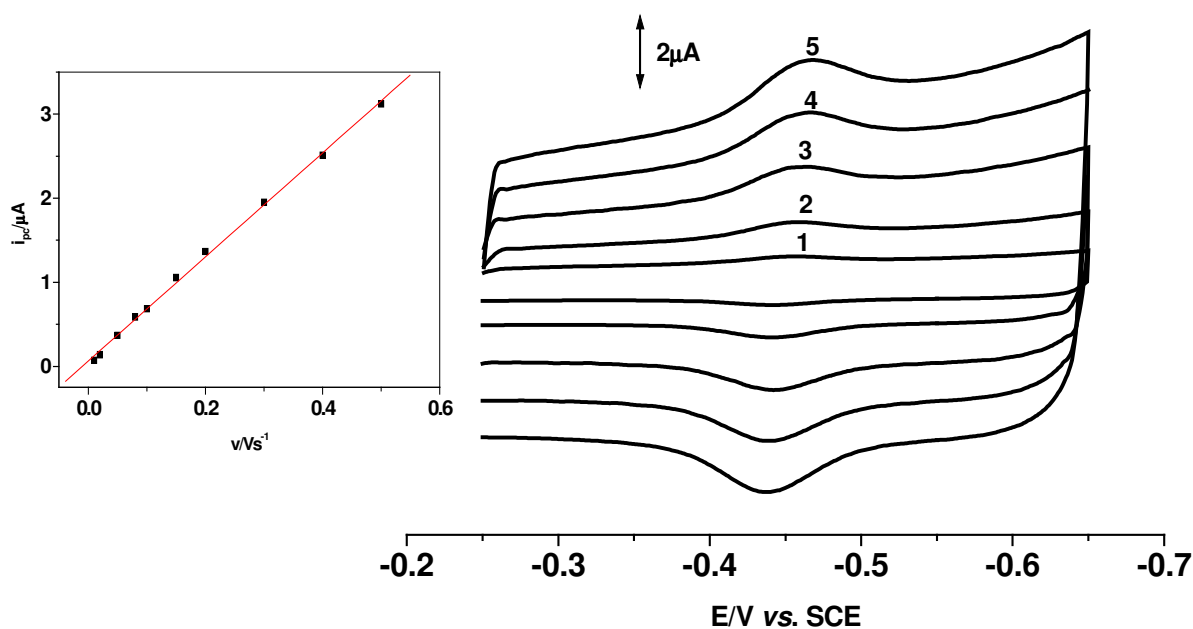


Fig.2. Cyclic voltammograms of glucose oxidase (1.0×10^{-4} M) at a SWNT-modified gold electrode in a 0.05M phosphate buffer solution (pH 7.0) at scan rates of (1) 0.02, (2) 0.05, (3) 0.10, (4) 0.15, (5) 0.20 Vs^{-1} . The inset is a plot of the reduction peak current i_{pc} against the scan rate.

Effect of pH on the Peak Current and Peak Potential of GOD at an SWNT Film-Modified Electrode

Figure 3 depicts a series of CVs of GOD collected from 0.05 M phosphate buffer solutions of different pH values. As can be seen, the peak potential of GOD is dependent on the solution pH. Within the pH range of 5.0-9.1, the peak potential shifts to the cathodic direction with a slope of 48 mV per decade of $[H^+]$. Therefore, it appears that there are two protons involved per transfer of two electrons. Thus, the electrode reaction could be described as below:



At about pH 7.0, the GOD redox peaks were found to best defined. Therefore, we fixed the solution pH at 7.0 for the investigations of the analytical performance of SWNT-modified electrodes covered with GOD.

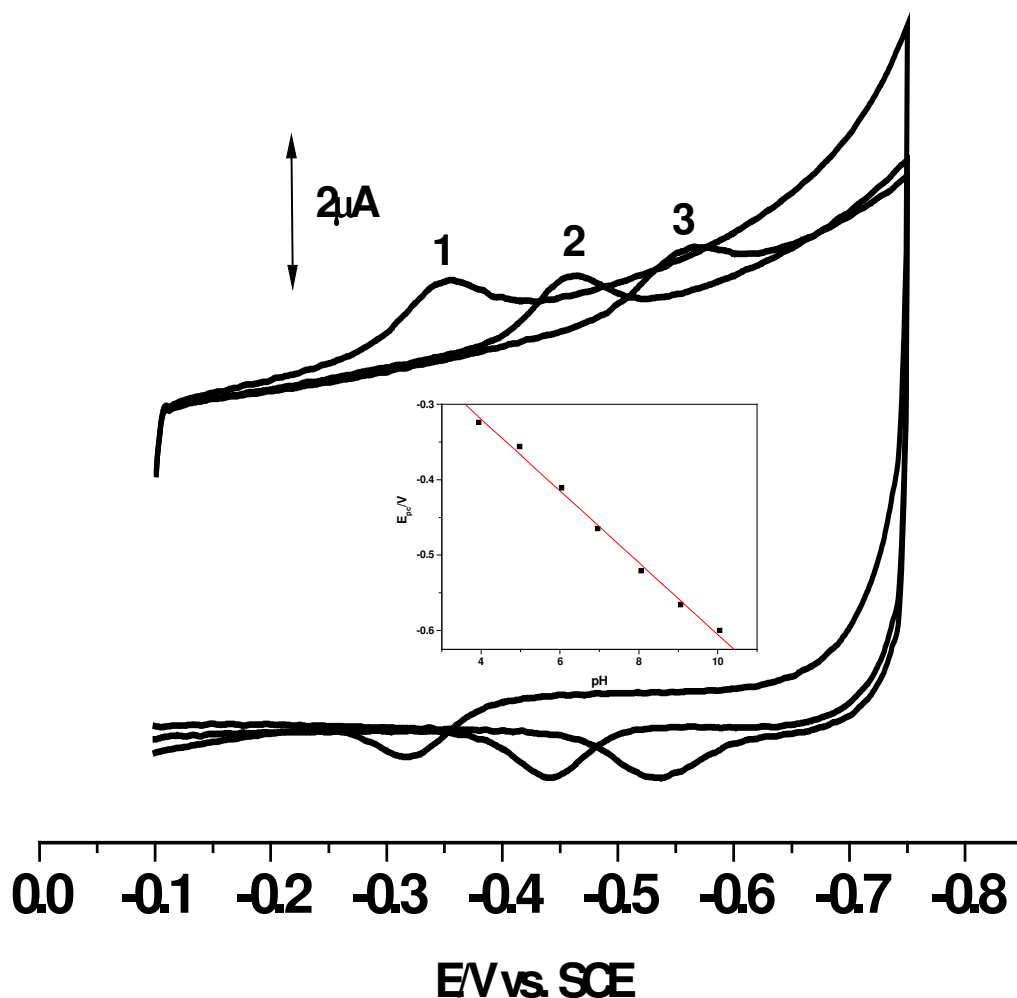


Fig.3. Cyclic voltammograms of glucose oxidase (1.0×10^{-4} M) at a SWNT-modified gold electrode in 0.05M phosphate buffer at pH values of (1)5.0, (2)7.0, (3)9.1. The inset shows the relationship between the reduction peak current E_{pc} and the solution pH value. The scan rate employed was $0.1V s^{-1}$.

Stability of the SWNT Film-Modified Electrode

The preparative procedure for forming SWNT-modified electrodes was found to yield highly repeatable GOD redox currents. For example, five SWNT-modified gold electrodes fabricated using the same protocol produced an average i_{pc} of 0.75 μA with a relative standard deviation (%R.S.D.) of 6.5%, when the GOD concentration was $1.0 \times 10^{-4} \text{ M}$ and v was 0.1 Vs^{-1} . Such a value is acceptable for most well-established analytical methods, indicating that the effective area constituting SWNTs for the GOD adsorption remains constant between preparations.

The surface coverage (Γ) of GOD on the SWNT Film-Modified Electrode

The surface coverage (Γ) of GOD was calculated. In order to obtain the effective surface area of SWNT, $\text{K}_3\text{Fe}(\text{CN})_6$ was used as a probe. CV experiments of 1mM $\text{K}_3\text{Fe}(\text{CN})_6$ at SWNT modified Au electrode were performed. For a reversible process, $i_p = (2.69 \times 10^5) n^{3/2} A D^{1/2} v^{1/2} C_0$ for $\text{K}_3\text{Fe}(\text{CN})_6$, $n=1$, $D=7.6 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, then the effective surface area of SWNT on the electrode could be calculated and 0.040 cm^2 was obtained. Then according to the coulometer charge in the cyclic voltammeter peaks of GOD/SWNT, the amount of GOD adsorbed on the SWNT surface could be also obtained. It was found that Γ is $5.1 \times 10^{-11} \text{ mol cm}^{-2}$, indicating that GOD maybe has a saturated monolayer adsorption on SWNT surface.

FT-IR spectra of GOD on the SWNTs Films

The adsorbed GOD still retains its specific enzyme activity, which is verified by FT-IR measurements. The amide I and II infrared bands have been widely used for monitoring conformational changes in proteins [40,41]. The amide I band ($1700\text{-}1600 \text{ cm}^{-1}$) is caused by C=O stretching vibrations of peptide linkages in the protein's backbone. The amide II band ($1600\text{-}1500 \text{ cm}^{-1}$) results from a combination of N-H in plane bending and C-N stretching of the peptide groups. As shown in Figure 4, two amide bands, within ranges of $1700\text{-}1600 \text{ cm}^{-1}$ and $1600\text{-}1500 \text{ cm}^{-1}$, were observed at both a GOD film cast onto a Si wafer and a SWNT film covered with GOD. The former (1652 cm^{-1} , amide I band) is caused by C=O stretching vibrations of peptide linkages in the GOD backbone, whereas the latter (1574 cm^{-1} , amide II band) results from a combination of N-H in-plane bending and C-N stretching of the peptide groups. A SWNT-modified surface did not produce any spectral absorption in the wavelength range. The presence of these two distinctive absorption bands in Figure 4 clearly suggests that the attachment of GOD onto SWNTs does not perturb the GOD conformations drastically. The small difference of the two spectra in Figure 4 indicated that GOD retained its native conformation in SWNT film despite the small perturbation. Purposely denatured samples of GOD showed completely different spectral characteristics in spectra in amide I and II regions.

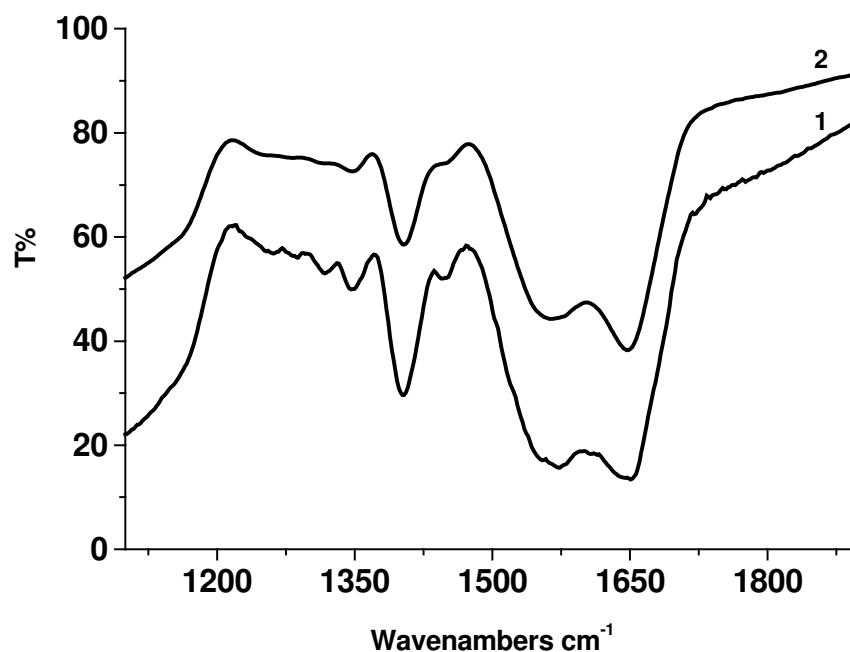


Fig.4. FT-IR spectra of a cast glucose oxidase film on a silicon wafer (1) and a glucose oxidase film covering a SWNT-modified silicon wafer(2).

It is well known that carbon nanotubes are promising materials as electrochemical mediators and enzyme stabilizers[35]. It is possible to adsorb a variety of enzymes on carbon nanotube while their specific enzyme activity were retained. Davis's group demonstrated that catalytic response at glassy carbon electrode modified with GOD-SWNTs (glucose oxidase immobilized on SWNTs) was observed upon the addition of glucose[42]. Zhao reported direct electrochemistry of horseradish peroxidase(HRP) at carbon nanotube powder microelectrode(CNTPME).Furthermore the adsorbing HRP still retains its catalytic activity to H₂O₂[43].The combination of carbon nanotube with redox active enzymes would appear to offer an excellent and convenient platform for a fundamental understanding of biological redox reactions as well as the development of reagentless biosensors and nanobiosensors.

Conclusions

This work demonstrates that direct electrochemistry of glucose oxidase can be conducted at SWNT-modified Au electrodes. A reversible reduction wave can be observed with E_{pc} at -0.465 V (vs. SCE) and ΔE_p of 23 mV at pH 7.0. The peak potential is pH-dependent and shifts to the cathodic direction by 48 mV per unit of pH. The cathodic peak current, i_{pc} , was found to be proportional to the scan rate, suggesting that the redox wave was given rise by the GOD adsorbate at the SWNTs. The specific enzyme activity of the GOD adsorbates at the SWNTs was found to

be retained. The results suggest that SWNT-modified electrodes covered with redox-active enzymes can retain the enzyme activities and provide an attractive route for the development of biosensors and nanobiosensors.

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Sample Availability: Available from the authors.