Optically Transparent Diamond Electrodes for UV-Vis and IR Spectroelectrochemistry

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No other material shows as much versatility as an electrode as does electrically conducting, chemical vapor deposited (CVD) diamond.[1,2] The material can be used in electroanalysis to provide low detection limits for analytes with superb precision and stability; for high-current density electrolysis (1-10 A/cm^2) in aggressive solution environments, without any microstructural or morphological degradation; as a corrosion-resistant electrocatalyst support; and as an optically transparent electrode (OTE) for spectroelectrochemical measurements. The purpose of this article is to introduce the reader to the fabrication and properties of diamond OTEs and to demonstrate two examples of UV-Vis and IR transmission spectroelectrochemical measurements made with this new material.

The use of electrically conductive diamond as an optically transparent electrode (OTE) is a new field of research.[3,5] Diamond possesses attractive qualities as both an electrode and an optically transparent material, making it an obvious choice for use as an OTE in spectroelectrochemical measurements. Diamond OTEs exhibit several technologically useful properties (1) the possibility of transmission measurements from the near-UV to the far-IR (0.225-100 µm); (2) low background current; (3) wide working potential window; (4) good responsiveness for many analytes without activation pretreatment; (5) electrical and optical stability in most aqueous and nonaqueous solution environments during both cathodic and anodic polarization ($\geq$ 10 mA/cm^2); and (6) resistance to fouling.

Diamond OTEs can be fabricated in several different forms, useful for transmission and or reflection measurements. Importantly, the optical and electrical properties can be engineered to varying degrees through adjustments in the CVD conditions. Diamond growth is often carried out in CH_4/H_2 source gas mixtures (~0.5%), at a system pressure of ca. 45 torr, a substrate temperature of ca. 800°C, and a total gas flow of ca. 200 sccm. Microwave- or hot-filament-assisted activation of the
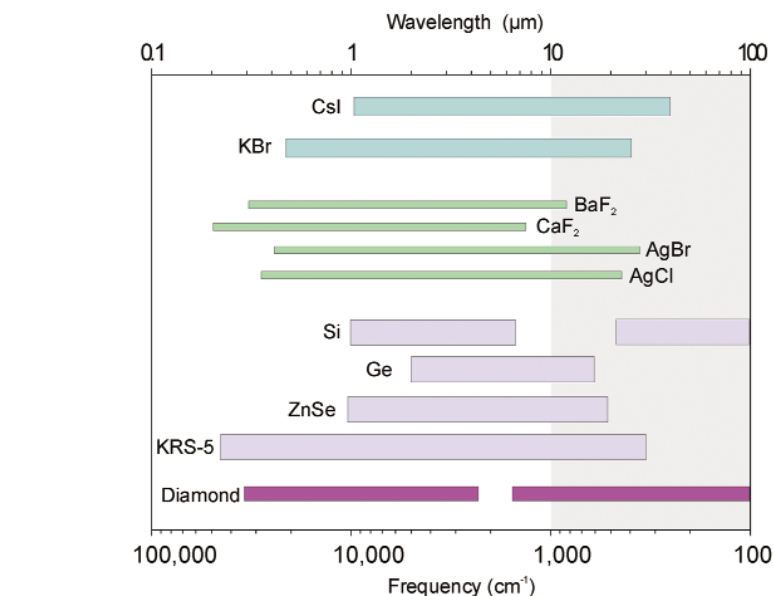

FIG. 1. Optical windows of different transparent materials.

source gases is typically used to produce the reactive growth precursors. Boron-doping can be accomplished by adding B_2H_6 to the source gas mixture.

One electrode form is a mechanically polished (~30 nm roughness), free-standing disc of diamond. Such a disc can be prepared by growing a thick film of diamond on a refractory metal substrate, like Mo. If the sample is cooled rapidly from the growth temperature, then the film will separate from the substrate due to stress (compressive) resulting from the difference in thermal expansion coefficients for diamond and the substrate. The polycrystalline disc is then mechanically polished smooth to reduce the surface roughness (i.e., light scattering). We previously reported on UV-Vis transmission spectroelectrochemical measurements of the aqueous redox analytes, ferri/ferrocyanide and methyl viologen, using such an electrode (8 mm diameter and 0.38 mm thick).[3]

Another electrode form is a thin film deposited on an optically transparent non-diamond substrate, such as undoped Si for IR or quartz for UV-Vis transmission spectroelectrochemical measurements. Diamond deposition on Si for IR OTEs is rather straightforward and involves growth conditions similar to those described above. The resulting

films are 2-4 µm thick with micrometer-sized grains of diamond randomly oriented over the surface. Martin and Morrison reported on a creative IR spectroelectrochemical approach for characterizing carbon-oxygen functional groups formed on the surface of diamond electrodes during anodic polarization, in which the OTE was a thin film of diamond deposited on undoped Si and employed in an internal reflection measurement.[4]

Deposition of thin films of diamond on quartz is a little more involved.[5] It is important to keep the diamond crystallite size smaller than the wavelengths of light to minimize scattering. This is achieved by mechanically polishing the quartz surface with diamond powder (10 nm) in order to produce a high density of scratches. This serves to increase the nucleation density such that small grains of diamond form in a continuous fashion over the substrate surface. The film thickness is 0.5-1 µm with aggregates of diamond grains ca. 100-200 nm in diameter. We recently described UV-Vis transmission spectroelectrochemical measurements of chlorpromazine (CPZ), using a thin film of diamond deposited on quartz.[5]

Figure 1 shows the optical windows, from 0.1 to 100 µm, for a number of

transparent materials. It is evident that diamond has the widest optical window of all. Furthermore, diamond is an outstanding OTE material because controlled electrical conductivity can be introduced through boron doping, the material can be deposited in a thin film form, and the material possesses superb chemical inertness and corrosion resistance in most aqueous and nonaqueous media.

The field of spectroelectrochemistry dates back to 1964 when the first work was reported by Kuwana, Darlington, and Leedy.[6] The authors described the use of indium tin oxide (ITO), coated on glass, as an OTE for UV-Vis transmission spectroelectrochemical measurements of several inorganic and organic redox analytes. The field has evolved over the years to encompass research on a variety of topics: new electrode development, thin-layer cell design, and construction. Additionally, many novel measurement schemes have been developed for material characterization, structure-function studies of biomolecules, and environmental-contaminant monitoring.[7-9] Several different OTEs have been used along the way, with the most common type being ITO.[7]

While highly functional for many applications, ITO has some material property limitations. These include (1) highly variable optical and electrochemical properties from source to source; (2) intolerance to cathodic polarization; and (3) instability during exposure to strongly acidic or alkaline media, and to some chlorinated organic solvents. In contrast, the optical and electrochemical properties of diamond OTEs are (1) reproducible from batch to batch and (2) very stable during either cathodic or anodic polarization in all types of chemical environments. Clearly, major attributes of diamond OTEs are the wide optical window and the reproducible and stable responsiveness, even in aggressive electrochemical environments.

Optical and Electrical Properties of Diamond OTEs

Several factors influence the optical transparency of CVD diamond in different regions of the electromagnetic spectrum.[10] These include (1) reflectance losses in the UV-Vis range due to a high refractive index (2.41 at 591 nm); (2) absorption attributable to the boron doping in the near-IR extending into the IR and visible spectral regions; (3) scattering losses in the UV-Vis range due to the rough, poly-
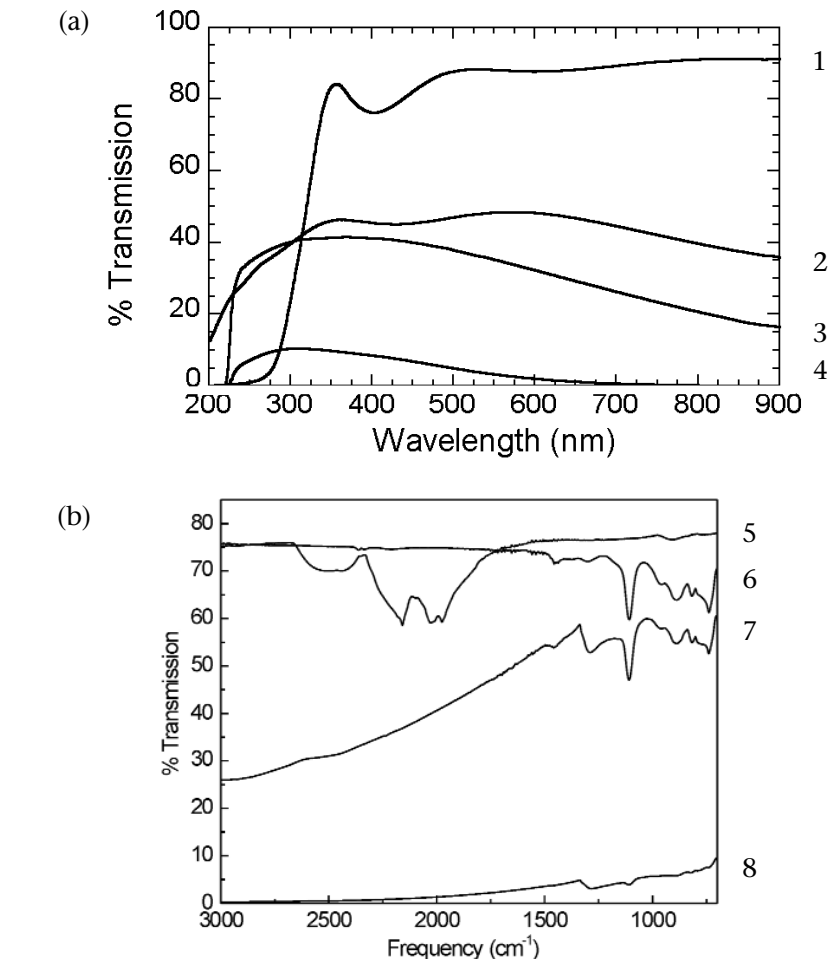

FIG. 2. Transmission spectra for different materials in the (a) UV-Vis and (b) IR regions of the electromagnetic spectrum. The electrodes in (a) are (1) a thin film of ITO on quartz, (2) a thin film of boron-doped nanocrystalline diamond on quartz, (3) a thin film of mechanically polished and boron-doped diamond on an optically pure, white diamond substrate, and (4) a free-standing, boron-doped, and mechanically polished diamond disc.

The electrodes in (b) are (5) an optically pure and mechanically polished white diamond disc, (6) an undoped and polished (both sides) Si substrate, and (7 and 8) moderately and heavily boron-doped microcrystalline diamond thin films deposited on the undoped Si.

crystalline surface of most films or scattering centers in the films; and (4) absorption by chemical impurities and defect centers, such as sp^2-bonded non-diamond carbon at extended defects and adventitiously incorporated nitrogen and silicon. A key to making a functional diamond OTE is obtaining a balance between the boron-doping level required for the desired electrical conductivity and the maintenance of sufficient optical transparency.[3,5]

Figures 2a and 2b show a series of transmission spectra for diamond OTEs in the UV-Vis and IR regions of the electromagnetic spectrum. Spectra for several different electrode formats are shown, for comparison. Figure 2a shows transmission spectra for thin films of (1) ITO on quartz, (2) boron-doped nanocrystalline diamond on quartz, (3) mechanically polished and boron-doped diamond on an optically pure, white diamond substrate, and (4) a free-standing,

boron-doped, and mechanically polished diamond disc. The ITO substrate has about 80% transparency at wavelengths in the visible region of the electromagnetic spectrum with an absorption edge starting at ca. 300 nm. The transmission of the boron-doped diamond thin film on quartz has an absorption edge at ca. 225 nm and a relatively constant transparency from 40 to 50% between 300 and 800 nm. The reduced light throughput in this region is attributable mainly to reflectance losses. Given the large refractive index, this is about the maximum transmission that can be expected for a thin film of diamond on quartz (for this boron-doping level, ~10^{19} B/cm^3, ~0.1 ohm-cm). The polished, boron-doped film deposited on the optically pure white diamond and the polished boron-doped, free-standing disc have lower levels of light transmission than the diamond/quartz OTE, with a continuous decrease in the
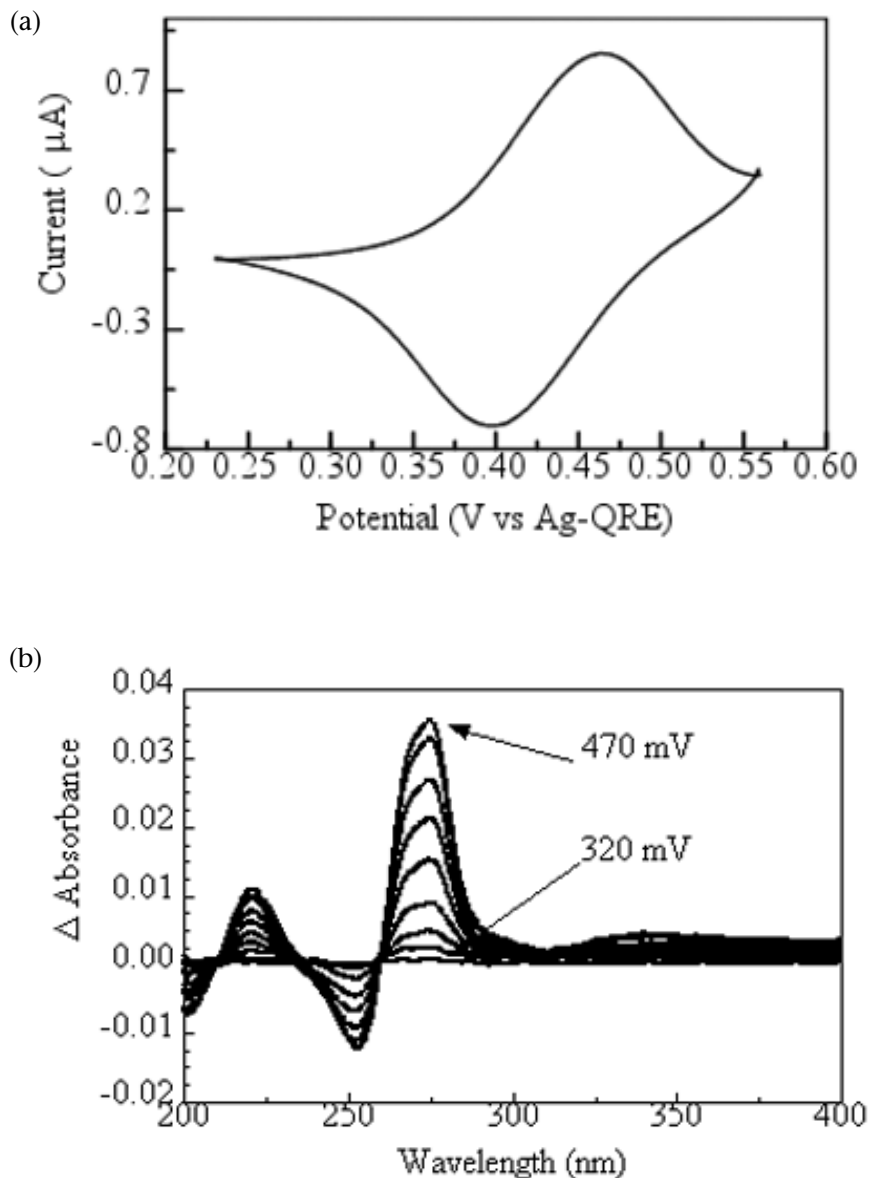
(a)

(b)

FIG. 3. (a) Background-corrected, thin-layer voltammetric i-E curve for a diamond/quartz OTE (see Fig. 2a, 2) in 0.1 mM CPZ + 10 mM H$_2$SO$_4$. Scan rate = 2 mV/sec. The film was deposited from a source gas mixture of 0.5% C/H and 10 ppm B$_2$H$_6$; (b) A series of UV-Vis absorbance difference spectra, using the same film, for 0.1 mM CPZ + 10 mM HClO$_4$, as the potential was stepped from 0.32 to 0.47 V vs. Ag-QRE. Reprinted with permission from Anal. Chem., **74**, 5924 (2002). Copyright (2002) American Chemical Society.

some weak absorption below 1200 cm^{-1}, the Si substrate possesses about 75% transmittance throughout the entire mid-IR. The reduced light throughput is due to relatively constant reflectance losses (~30%) over the entire wavelength range.

When boron is introduced into the lattice, creating a conductive OTE material, the transparency decreases as shown in Fig. 2b (7 and 8), particularly above 1500 cm^{-1}. Introduction of substitutional boron breaks the lattice symmetry, resulting in increased absorption due to impurities and one-phonon modes.[11] Specifically, boron gives rise to absorption bands at 2460 and 2790 cm^{-1}, due to the electronic transitions from the ground to the first and second excited states of the dopant atoms, respectively.[12] However, for more heavily doped films, a broad continuum develops beyond 2000 cm^{-1}, as a result of the interaction of the boron centers, resulting in boron acceptor level degeneracy. The mode at 1290 cm^{-1} is attributed to the one-phonon vibronic absorption induced by the boron acceptor centers.[12] Despite the marked decrease in transmittance observed in the region above 1500 cm^{-1}, from boron incorporation, it is important to note that the moderately doped film retains a high level of throughput in the region below 1500 cm^{-1}.

The electrical properties of the diamond films or free-standing discs are largely determined by the boron-doping level. Resistivities of useful diamond OTEs are in the range of 0.5 to 0.05 Ω-cm. Boron-doping levels, associated with this resistivity, are ca. 1-10 x 10^{19} B/cm^3, as determined by boron nuclear reaction analysis measurements. Very preliminary Hall effect measurements for the diamond/quartz (Fig. 2a, 2) and diamond/Si (Fig. 2b, 7) OTEs have revealed carrier concentrations between 10^{16} and 10^{18} cm^{-3} and carrier mobilities (holes are the majority carrier in boron-doped films) of 1 to 100 cm^2/V-s.

Transmission Spectroelectrochemical Measurements

One organic redox system that we have studied by transmission spectro-electrochemical measurements is chlorpromazine (CPZ).[5] The electrochemistry and spectroscopy of CPZ have been investigated extensively over the years.[13] Figure 3a shows a cyclic voltammetric (background corrected) i-E curve for 100 µM CPZ + 10

transmitted light at longer wavelengths. This results from IR absorption by the boron acceptor band which can extend into the visible, and this is the reason such films appear blue. The transmission in the far-visible and near-IR regions decreases proportionally with the boron-doping level.

Figure 2b presents IR transmission spectra for (5) an optically pure and mechanically polished white diamond disc, (6) an undoped and polished (both sides) Si substrate, and (7 and 8) moderately and heavily boron-doped

microcrystalline diamond thin films deposited on the undoped Si. The white diamond is relatively free of structural defects and chemical impurities. There is reduced transparency between 2500 and 1500 cm^{-1} due to the two-phonon absorption. Diamond films with more structural defects and chemical impurities lead to loss of crystal symmetry. This causes a more intense one-phonon absorption between 1500 and 1000 cm^{-1} and increased absorption between 3000 and 2700 cm^{-1}, due to vibrations of C-H bonds. With the exception of

mM HClO$_4$. The measurement was made in a specially designed, thin-layer electrochemical cell with a path length of 150 μm and a cell volume of 5 μL.[5] The scan was initiated at 0.20 V and scanned in the positive direction at 2 mV/s. Well-defined oxidation and reduction peaks are observed, which correspond to the following electrochemically reversible redox reaction:

$$CPZ \rightleftharpoons CPZ^{\bullet +} + e^-$$

A subsequent one-electron transfer occurs at more positive potentials, ~0.9 V, to form the dication, CPZ^{+2}, which is quickly hydrolyzed.[13] The electrode reaction kinetics for this redox system (CPZ/CPZ$^{\bullet +}$) are mainly influenced by the density of electronic states at the formal potential.[14] Rapid electrode-reaction kinetics have been observed for boron-doped diamond electrodes, with no evidence of any molecular adsorption.[14] The Q_p^{ox}/Q_p^{red} ratio for the CPZ/CPZ$^{\bullet +}$ redox reaction is ca. 1. The i_p^{ox} and i_p^{red} values varied linearly with the scan rate, while Q_p^{ox} and Q_p^{red} were independent of scan rate. These trends are predicted for thin-layer voltammetric behavior.

Figure 3b presents a series of potential-dependent UV-Vis difference spectra for CPZ during the one-electron transfer reaction to form CPZ$^{+\bullet}$. CPZ has an absorbance maximum at 253 nm, due to a $\pi \rightarrow \pi^*$ transition ($\varepsilon^\circ \sim$ 10,000 AU cm^{-1} M^{-1}), while the radical cation (CPZ$^{+\bullet}$) has a maximum at 275 nm, presumably also due to a $\pi \rightarrow \pi^*$ transition ($\varepsilon^\circ \sim$ 20,000 AU cm^{-1} M^{-1}).[15] In neutral solution, the radical cation rapidly disproportionates, limiting its spectroscopic observation. Therefore, measurements were carried out at pH 2, a value at which the radical cation is stable. The spectra were obtained after 1 min equilibration times at each potential. It can be seen that, as the potential is shifted stepwise from 320 to 470 mV, the peak at 253 nm progressively decreases and the peak at 275 nm increases. The spectra shown were background-corrected by subtracting the spectrum for the fully reduced CPZ. When overlaid, the spectra show well-defined isosbestic points. An isosbestic point near 260 nm indicates that the species responsible for the absorbance peaks, on either side of the point, are stoichiometrically related. In this case, these peaks are attributed to CPZ and CPZ$^{+\bullet}$. The spectral trends were completely reversible with cycling.

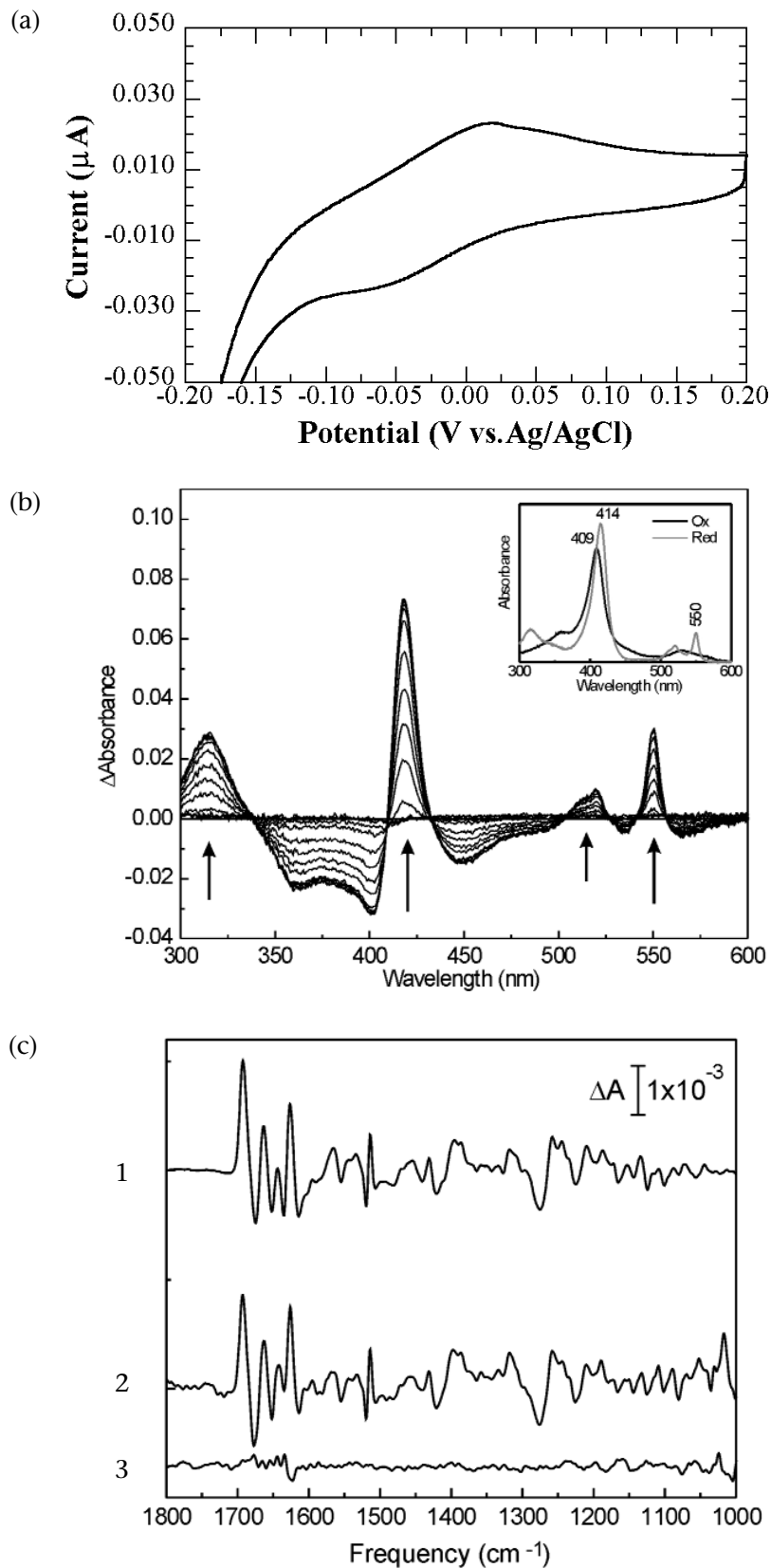Diamond OTEs are also useful for studying the electrochemical and opti-

Fig. 4. (a) Cyclic voltammetric i-E curve for 25 mM horse heart cytochrome c in 1 mM Tris HCl buffer, pH 7, containing 20 mM NaCl at a boron-doped, free-standing diamond disc OTE (see Fig. 2a, 4); (b) UV-Vis reduced minus oxidized (at 0.40 V) difference absorbance spectra for horse heart cytochrome c collected at 0.050 V intervals from 0.30 to –0.20 V using the diamond disc OTE. The inset depicts the absolute reduced (grey line) and oxidized (black line) spectra. The solution contained 0.5 mM cytochrome c in 100 mM phosphate buffer at pH 7.4; (c) Reduced (-0.20 V) minus oxidized (0.30 V) electrochemical FTIR difference spectra for cytochrome c acquired at (1) an Au grid OTE and (2) a diamond/Si OTE (see Fig. 2b, 3); (3) A noise spectrum is shown for the cell containing the diamond OTE. The solution contained 3 mM cytochrome c, 0.3 M NaCl, 10 mM Tris HCl at pH 7.

cal properties of important biomolecules, such as cytochrome c. We recently reported that boron-doped microcrystalline diamond thin-film electrodes are quite responsive to horse heart cytochrome c, exhibiting a very active and stable cyclic voltammetric response without any pretreatment or surface modification.[16] Heterogeneous electron transfer rate constants in the mid to high 10^{-3} cm/s range are typical for both boron-doped microcrystalline and nanocrystalline thin films. The observation of a nearly reversible, diffusion-controlled response at a hydrophobic (hydrogen-terminated) and uncharged (no ionizable surface carbon-oxygen functional groups) electrode contrasts with the conventional wisdom regarding heterogeneous electron transfer of this protein, as the electrode kinetics are known to be strongly dependent on a combination of interfacial electrostatic and chemical interactions at other electrode surfaces.[17]

Figure 4a shows a cyclic voltammetric i-E curve for 25 μM horse heart cytochrome c in 1 mM Tris HCl buffer (pH 7) containing 20 mM NaCl. The measurement was made in a specially constructed, thin-layer, electrochemical cell with a path length of approximately 100 μm and a cell volume of approximately 6 μL. The diamond OTE was a free-standing diamond disk (380 μm thick and 8 mm in diameter). The scan was initiated at 0.15 V and recorded at 2 mV/s. The oxidation and reduction peaks present at –0.075 and 0.00 V (ΔE_p) are not as well-defined as they are for other redox systems (e.g., ferrocene) at this same electrode. The cathodic current at –0.15 V is believed to be due to some residual oxygen reduction, as the thin-layer cell could not be efficiently deoxygenated with nitrogen.

Figure 4b shows a series of UV-Vis difference spectra (reduced minus oxidized) for 500 μM cytochrome c in 10 mM Tris HCl, pH 7, buffer containing 0.3 M NaCl. The measurements were made in the same thin-layer cell used for the voltammetry in Fig. 4a. The series of spectra were collected by measuring the absorption spectrum for the progressively reduced form of the protein in 50 mV increments from 0.30 to –0.20 V and subtracting the spectrum for the fully oxidized form at 0.40 V. The spectra were obtained after a 1 min equilibration time at each potential. A series of positive and negative peaks are observed at the different potentials. The arrows depict the positive peaks that correspond to the reduced form of the protein, and the peaks increase in amplitude as the potential is made more negative.

The UV-Vis spectra of heme-containing proteins, such as cytochrome c, contain two major bands—the Soret and α-bands. The most intense of these two is the Soret band, which occurs between 400 and 450 nm, depending on the nature of the heme iron and oxidation state of the protein.[18] Both bands are attributed to the π→π* transitions of the heme, and are, therefore, a very sensitive indicator of the heme iron oxidation state. The spectra presented, specifically between 400 and 600 nm, are the same as those reported previously[19] and indicate that direct electrochemical titration of this protein is possible. It is important to note that the response is stable and reproducible with repeated cycling. The stable isobestic points further indicate that no protein denaturation occurred.

One additional spectral feature to be pointed out is the accessible wavelength range possible with the diamond OTEs. The spectrum shows that the region between 200 and 400 nm contains two absorption bands, the N and L bands, which, like the Soret and α-bands, are assigned to π→π* transitions of the heme Fe.[20] Many characteristic amino acid absorption transitions occur below 400 nm, such as tyrosine absorption at 280 nm. This range has been exploited in spectroelectrochemical measurements of ferrocene at diamond OTEs.[21]

The large Soret bands report on the oxidation state of the heme Fe, but the absorbance of the α-band is routinely used to calculate the cytochrome c concentration and to monitor heme reduction.[22] This is due to the fact that the 550 nm absorption band is characteristic of the reduced form of the protein. It is not influenced by nearby, overlapping bands, as is the case for the Soret region where the oxidized and reduced forms give rise to strong, broad absorption bands of nearly equal intensity. The absorbance intensity at 550 nm, obtained from the direct redox titration of cytochrome c as a function of the electrode potential, was found to be a near perfect fit to the Nernst equation. The formal reduction potential determined from the plot was 0.072 V, which is in good agreement (± 0.01 V) with the accepted value of 0.06 V (vs. Ag/AgCl).[23]

Figure 4c (2) shows a reduced (-0.20 V) minus oxidized (0.30 V) IR difference spectrum for 3 mM horse heart cytochrome c in 10 mM Tris HCl buffer, pH 7 at a diamond/Si OTE. All spectra presented represent an average of 800 scans collected at 10°C with a path length of 10 μm. The electrochemical difference IR spectrum has previously

been reported using an Au minigrid OTE.[19] This enabled us to evaluate the performance of the new diamond OTE with respect to that of a conventional OTE. Figure 4c also contains (1) our own spectroelectrochemical measurement of the protein using an Au minigrid OTE. Comparison of the spectra for the diamond/Si and Au OTEs reveals excellent agreement in that all features are retained.[19] There are many peaks in the difference spectrum representative of amino acid side chain and peptide backbone vibrations. A comprehensive interpretation of the spectrum is beyond the scope of this manuscript. Finally, fig. 4c shows (3) the background-noise spectrum for the diamond OTE. It is clear that the background signal is flat and relatively featureless, even in the areas of strong water absorbance. ∎

Conclusions

Diamond OTEs offer the possibility of sensitive, reproducible, and stable spectroelectrochemical measurements in both the UV-Vis and IR regions of the electromagnetic spectrum. The optical and electrochemical responses are reproducible from batch to batch (i.e., at constant deposition conditions) and stable during anodic and cathodic polarization in aggressive chemical environments. Optical transparencies of ca. 50% between 300 and 900 nm and greater than 50% below 1500 cm^{-1} can be achieved with thin films possessing low electrical resistivity (≤ 0.1 ohm-cm).

Acknowledgments

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