SUPPLEMENTARY INFORMATION

CHITOSAN-COATED ELECTRODES FOR BIMODAL SENSING. SELECTIVE POST-ELECTRODE FILM REACTION FOR SPECTROELECTROCHEMICAL ANALYSIS

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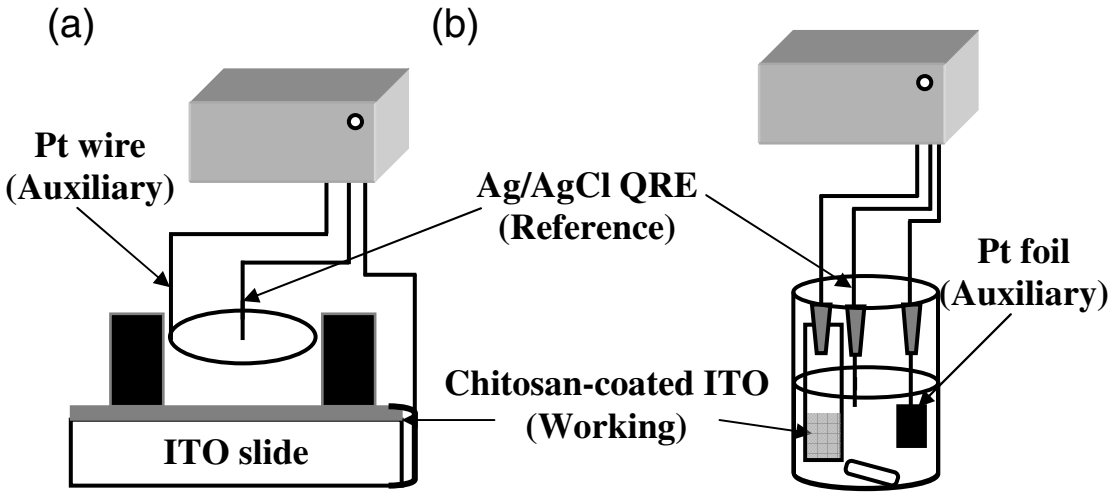
Experimental Systems for Electrochemical Analysis

Electrochemical measurements such as cyclic voltammetry (CV), amperometric current vs. time (*i-t*) measurements, and chronocoulometry were carried out with a CHI627C Electrochemical Analyzer (CH Instruments, Inc., Austin, TX). Measurements were performed with three-electrodes using experimental systems illustrated **Scheme S1**. **Scheme S1a** shows an electrochemical cell that consists of an open-end rubber cylinder (volume 0.6 ml) clamped on top of the chitosan-coated ITO slide. The area exposed to the analyte solution was 0.5 cm^2. We also used the more conventional three electrode system shown in **Scheme S1b**. Details of experimental conditions are provided in the text and figure captions. The Ag/AgCl quasireference electrode (QRE) was prepared by immersing a piece of Ag wire into concentrated HCl for 5 hours.

Scheme S1. Experimental systems used for this proof-of-concept study.



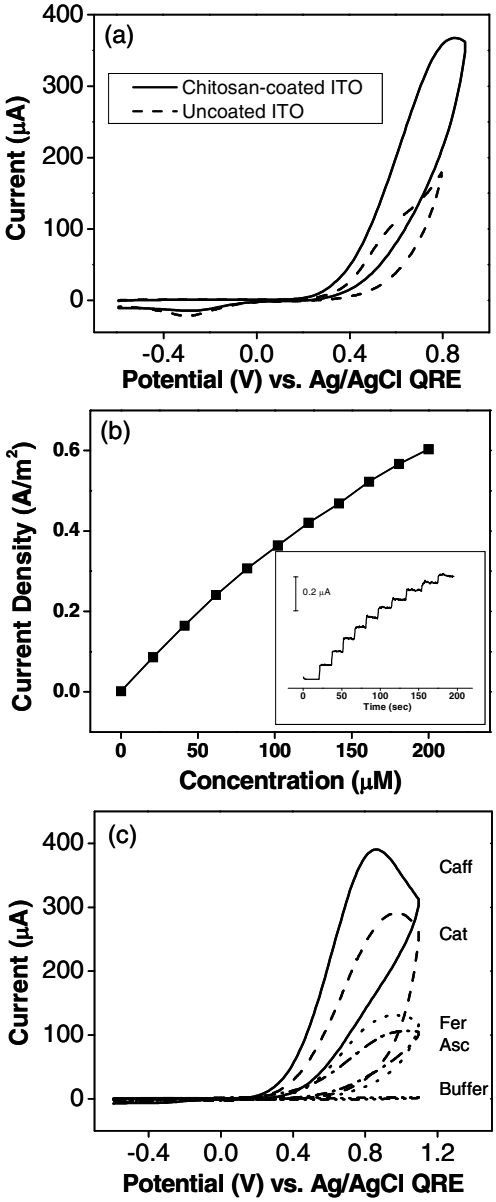
Initial Studies with Chitosan-Coated ITO Electrodes - Permeability of Chitosan Film

Scheme 1 (in the text) illustrates that the bimodal sensing approach requires the chitosan film to be permeable to the electrochemically-active solutes. To demonstrate permeability of the chitosan film, we compared the oxidation of caffeic acid by a chitosan-coated ITO electrode with oxidation by an uncoated ITO electrode. Specifically, we used the experimental system in Scheme S1a and generated cyclic voltammograms (CVs) for a 2.5 mM solution of caffeic acid. **Figure S1a** shows two differences were observed in the CV. First, the anodic currents for the chitosan-coated electrode are larger than for the uncoated electrode. While this observation demonstrates that caffeic acid can readily diffuse through the chitosan film, it is not clear why oxidation is enhanced for the chitosan-coated electrode. Possibly, caffeic acid is preconcentrated in the chitosan film. The second observation in Figure S1a is the nearly complete absence of a reduction peak in the CV for the chitosan-coated electrode. This observation is consistent with the hypothesis that the oxidation product generated in the forward scan rapidly reacts with the chitosan film and is unavailable for reduction in the reverse scan.

To further examine the electrochemical characteristics of the chitosan-coated ITO electrode, we generated a standard curve for caffeic acid. Specifically, we used the experimental system of Scheme S1b and stirred the buffer solution (5.0 mL) while applying a constant voltage (0.8 V) to the chitosan-coated ITO electrode. Aliquots of concentrated caffeic acid (20 μl; 5.0 mM) were incrementally added as illustrated by the inserts in **Figure S1b**. The correlation between the steady state current and caffeic acid concentration is shown in Figure S1b, which illustrates that under these experimental conditions, micromolar concentrations could be detected. This result indicates that coating the electrode with chitosan does not interfere with the characteristic advantages of electrochemical analysis for speed and sensitivity.

Next, we compared the electrochemical oxidation of the four solutes by the chitosan-coated ITO electrodes. The CVs in **Figure S1c** show that oxidation of the individual phenols begins at about 0.4 V, and that caffeic acid is oxidized at the lowest potential followed by catechin and then ferulic acid. Figure S1c also shows that the non-phenol ascorbic acid is oxidized at the same potential as the phenols. The important conclusion from Figure S1 is that the chitosan film is permeable to all the phenols tested, and to ascorbic acid.

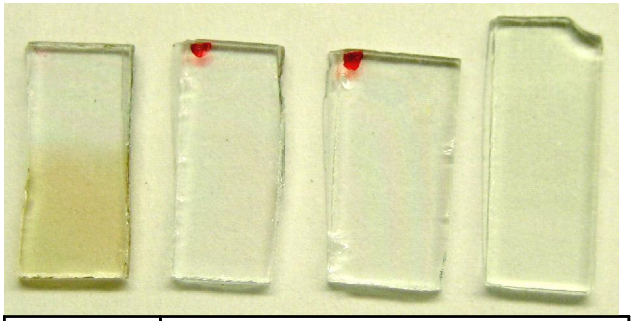
Figure S1. Initial results with chitosan-coated ITO electrode. (a) CV for caffeic acid (2.5 mM) oxidation by chitosan-coated and uncoated ITO electrode demonstrates that caffeic acid can diffuse through the chitosan film. Voltage measured against a quasi reference electrode at a scan rate of 0.1 V/sec. (b) Standard curve for the electrochemical analysis of caffeic acid by anodic oxidation at constant voltage (0.8 V). (c) CV for the four analytes (2.5 mM) and the buffer solution lacking analyte (scan rate 0.1 V/sec).



Initial Studies to Demonstrate Color-Forming Post-Electrode Film Reaction

To demonstrate that the film reaction is selective for oxidized phenols relative to the un-oxidized phenols, we anodically oxidized caffeic acid (1.0 mM) at 0.8 V for 5 min using a chitosan-coated ITO electrode in the experimental system of Scheme S1b. The photograph in **Figure S2** shows a considerable color change for this chitosan-coated electrode compared to a control in which a chitosan-coated electrode was contacted with caffeic acid in the absence of an applied voltage, or for controls in which reactions were performed in the absence of either caffeic acid or chitosan.

Figure S2. Post-electrode reaction between oxidized phenol and chitosan confers color to the film. Caffeic acid (1.0 mM) was oxidized (0.8 V for 5 minutes) by a chitosan-coated ITO electrode, and the photograph shows the color of the resulting film was brown compared to controls that lacked applied voltage, caffeic acid or chitosan.

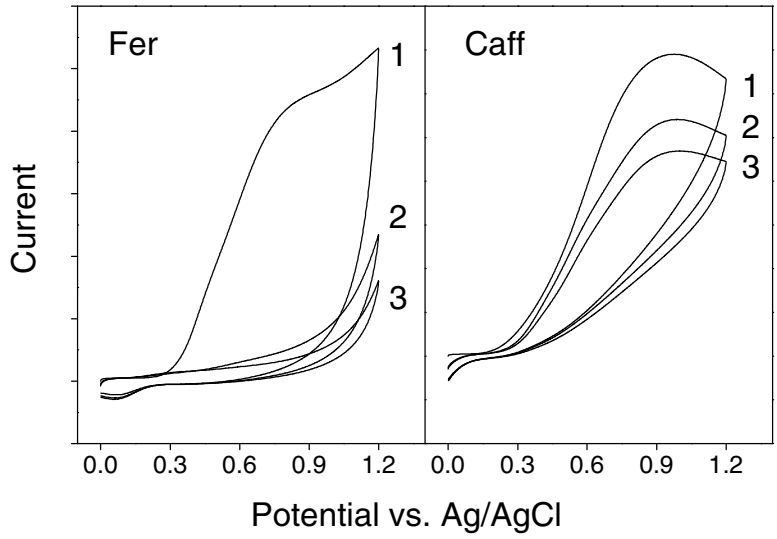


Sample	**Controls**		
Chitosan	Chitosan	Chitosan	-
Caff	Caff	-	Caff
21.5 C/m^2	-	5.5 C/m^2	50 C/m^2

Electrode Passivation During Oxidation of Ferulic Acid.

We believe that the non-linear response of ferulic acid in **Figure 7** of the paper is due to electrode passivation by this phenol. Passivation is indicated by the results in **Figure S3** which show a dramatic decrease of signals after the first scan with a solution of ferulic acid (1 mM). For comparison, the oxidation of caffeic acid shows a less significant decrease in oxidation upon three sequential cycles.

Figure S3. Three consecutive CVs of 1 mM ferulic acid (Fer) and caffeic acid (Caff) on ITO-coated glass slides demonstrate that electrode passivation is more significant for Fer than Caff. Scan rate=0.1 V/s.



Peak Positions Used for Analyzing XPS Spectra

Table S1. XPS binding energy assignment. The spectra of these samples are shown in Figure 4 in the text. Unless specified, the films were examined at a 90° take-off angle.

Region	Assignment	Chitosan (acidic)	Chitosan (neutralized)	Caffeic-acid modified chitosan (acidic)	Caffeic-acid modified chitosan (90°)	Caffeic-acid modified chitosan (30°)
N 1s	C=N	-	-	398.8	-	398.6
	R-NH_2	399.4	399.0	399.4	399.1	399.4
	NHCO-	400.4	400.0	400.4	400.1	400.4
	R-NH_3^+	401.7	-	401.5	-	-
C 1s	sp^2 HC	-		284.1	-	284.1
	sp^3 HC	284.6	284.6	284.6	284.6	284.6
	C=N	-	-	285.7	-	285.6
	C-OH/C-O-R	286.4	286.1	286.2	286.2	286.2
	O-C-O	288.0	287.7	287.5	287.8	287.3
	COOH	-	-	288.6	-	288.3