

Electronic Supplementary Information

Additional chemical evidence is provided that products generated from the electrochemical oxidation of dopamine can react with chitosan. For this, a dopamine solution (1M, pH 7.5) was electrochemically oxidized (4 mA/cm² for 6 min) under different conditions using large (millimeter scale) electrodes. When dopamine was oxidized in the absence of chitosan (i.e., the electrode was not coated with chitosan), Figure 1A shows the solution's UV-Vis absorption increased substantially. This increase is consistent with the formation of oligomeric and polymeric phenols. Electrochemical oxidation using a chitosan-coated electrode as the anode was also performed with the same current density and time (and presumably the same rate and extent of dopamine oxidation). Figure 1A shows a considerably smaller increase in UV-Vis absorption when the dopamine solution was oxidized by the chitosan-coated electrode. This difference in UV-Vis absorption suggests that products generated by dopamine's oxidation do not appear in solution because they undergo reaction with the chitosan film.

For comparison, oxidation reactions with ascorbic acid were also performed under same reaction condition as for dopamine. Ascorbic acid is the common species that interferes with dopamine's electrochemical detection from biological samples^{1, 2}. Figure 1B shows that oxidation of the ascorbic acid increases the solution's UV-Vis absorption. However absorption spectra of the oxidized solutions are similar regardless of whether oxidation is performed by the uncoated electrode or the chitosan-coated electrode. The similarity in solution absorption suggests that products generated by ascorbic acid's oxidation do not react with the chitosan film.

To complement the data from the solution, the chitosan films (~ 30µm thick) were examined after peeling them from the electrodes. The chitosan film that had been incubated with dopamine was observed to be brown in color and Figure 2 shows it has a broad UV-Vis spectrum. This spectrum is consistent with reactions between oxidized phenols and chitosan³⁻⁵. In contrast, the chitosan film incubated with ascorbic acid remained transparent and the spectrum in Figure 2 shows little UV-Vis absorption of this film. After all measurements were complete, the chitosan films were placed in an acidic solution of pH 3.5 (chitosan that is not crosslinked dissolves below pH of 6.5). The film incubated with dopamine was insoluble, while the film incubated with ascorbic acid dissolved. Together, these results provide chemical evidence that oxidation products of dopamine, but not ascorbic acid, react with the chitosan film.

References

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