ADVANCED MATERIALS

Supporting Information

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Effects of Interfacial Redox in Mussel Adhesive Protein Films on Mica

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***Supporting Data for adma.201003580*: Effects of interfacial redox in mussel adhesive protein films on mica**

By *Jing Yu*, *Wei Wei*, *Eric Danner*, *Jacob Israelachvili*, and *J. Herbert Waite**

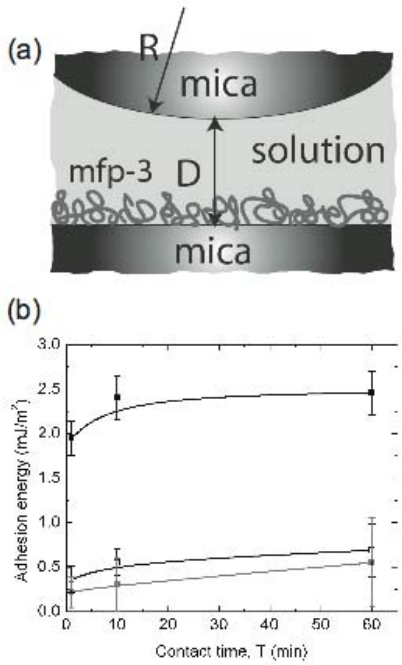

Figure S1. Asymmetric approach-separation cycles of mfp-3 on mica surfaces. a) Schematic of the surfaces in the SFA experiments in an asymmetric configuration used to measure the adhesion of mfp-3 to mica. b) The adhesion energy of the mfp-3 film and mica as a function of contact time at pH3, 5.5 and 7.5. At all pHs tested, the adhesion energy slightly increases with contact time. Error bars are the standard deviation of 9-12 measurements for 1 min test and 4-6 measurements for 10 min and 60 min test.

The adhesive strength of a mfp-3 film to mica was found to increase with the duration of contact to both mica surfaces. When the two surfaces were left in contact for 10 min, the adhesion energy increased to E_{ad}= -2.4 mJ/m^2. However, there was no significant difference in adhesion energy between 10 min and 60 min contact time, indicating that the adhesion energy plateaus rapidly. The increase of adhesion energy with contact time may be due to the rearrangement of the dopa residues in mfp-3 chains under confinement and this hypothesis is certainly undergoing further scrutiny. After short contact times, the dopa residues are likely to be orientated in all directions so that some of them are not able to bind to the other mica surface due to steric entanglements. Given enough contact time, the protein chains rearrange themselves and more dopa residues can adhere to the other mica surface.

Another plausible explanation is that since the protein film was deposited on one side before the SFA experiment, most or all dopa residues might adhere to the first mica surface during a short time contact. A longer contact time gives the dopa residues a better chance to flip over to the other mica surface. Therefore the system approaches the equilibrium state. Both explanations could lead to a higher adhesive strength with a longer contact time. Once the system reaches its equilibrium state, the strength of adhesion no longer increases but reaches a plateau. At both pH 5.5 and 7.5, the adhesive strength is found to slightly increase with contact time, but remains an order of magnitude lower than the strength measured at pH 3. At present we prefer the first explanation that only some dopa residues adsorb to the first surface and the remainder is unbound. Bell theory and experiments predict that bound bidentate dopa remains bound and safe from oxidation (see text). Unbound dopa in contrast is free to bind the other surface but only at low pH and after protein rearrangement. As the pH is raised from 3 to 5.5 to 7.5, more unbound dopa becomes oxidized to nonadhesive quinones.

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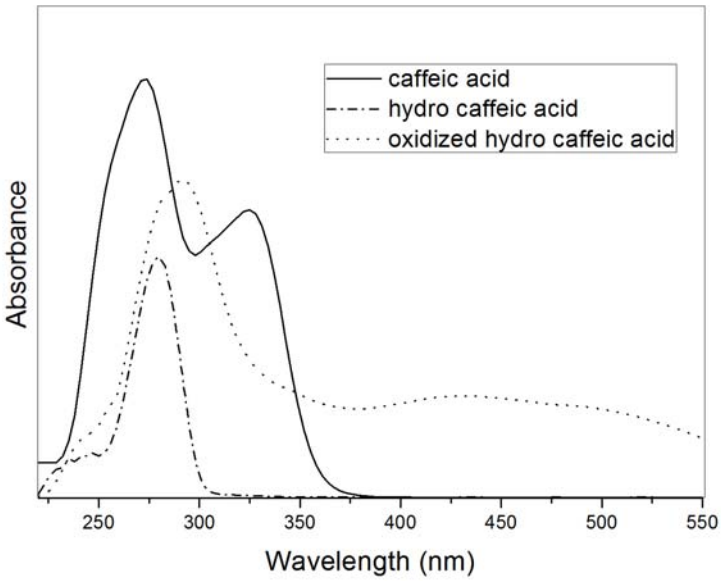
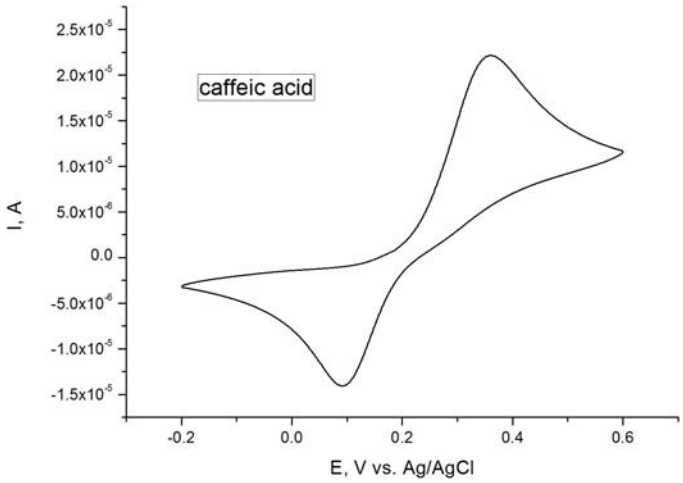


Figure S2. UV-Vis spectra of low molecular weight analogs of dopa (hydrocaffeic acid), Δ-dopa (caffeic acid), and dopa-quinone (periodate oxidized hydrocaffeic acid). All standard concentrations were 0.10 mM aqueous buffer solution 0.1 M sodium acetate and 0.25 M KNO_3 at pH 5.5.

(a)



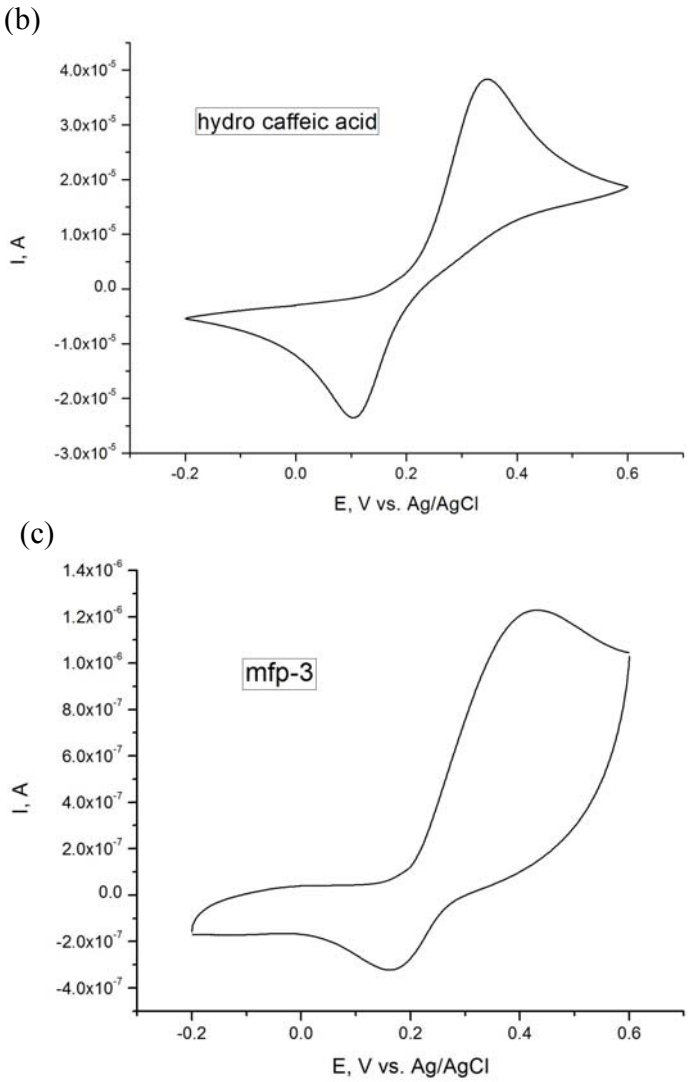


Figure S3. Cyclic voltammograms of a) caffeic acid; b) hydrocaffeic acid in pH 5.5 water/ ethanol (v:v= 1:1) solution containing 0.1 M sodium acetate and 0.25 M KNO_3, c) mfp-3 in pH 5.5 aqueous buffer solution containing 0.1 M sodium acetate and 0.25 M KNO_3, under argon; scan rate: 0.3 V/s vs. Ag/AgCl.

Cyclic voltammetry. Cyclic voltammetry (CV) was performed using a CIH 500/A electrochemical workstation from CH Instruments Inc. These analyses were carried out using three-electrode cell, a Pt wire as the counter electrode, a Ag/AgCl reference electrode calibrated with a 5 mM solution of Fc/Fc+ in 0.1 M TBAP/acetonitrile (ACN) as electrolyte solution and a glassy carbon working electrode. We intended to use CV to prove the two-step oxidation of dopa in mfp-3, which are from dopa to dopaquinone and

dehydrodopa to dehydrodopaquinone, respectively. Unfortunately, when scanning the voltage from -0.2 V to 0.6 V, oxidative peaks of caffeic acid and hydrocaffeic acid were barely indistinguishable (Fig S4 a) and b) 0.36 V for caffeic acid and 0.35 V for hydrocaffeic acid). Thus it is reasonable to suppose that mfp-3 has two overlapping oxidation peaks corresponding to dopa and Δ-dopa.

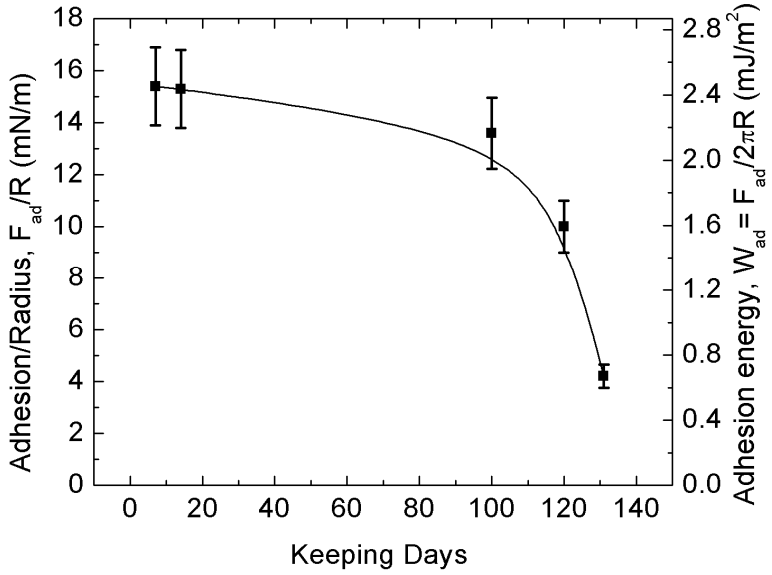


Figure S4. The adhesion of mfp-3 decreases with the duration of storage of mfp-3. All the adhesion forces were measured with 1 min contact time. Error bars are the standard deviation of 9-12 measurements.

The adhesion of mfp-3 is also correlated to the freshness of the protein. Figure S3 shows the adhesion versus the storage time using the same batch of purified mfp-3, which was stored in pH 3 buffer and in a -50 ^{o}C freezer. Freshly purified protein showed very strong adhesion at pH 3, and the adhesion could be preserved for about 3 months without significant decrease. However, after about 100 days, the protein started to lose its adhesive ability and thereafter showed a rapid decrease of adhesion. The adhesion of mfp-3 measured after 130 days storage is only about 25% of its original adhesion. This could be due to the gradual degradation of mfp-3 during storage and/or the slow

oxidation of dopa during storage. Mfp-3 possibly undergoes the same slow oxidation during storage.