Supporting Information

Mussel-inspired Chemistry for Robust and Surface Modifiable Multilayer Films

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Figure S1. FTIR spectra of PAA and PAA-dopamine.

Verification of Amide Bond Formation between PAA and Dopamine. As shown in Figure S1, pure PAA presents a strong peak at 1710 cm$^{-1}$, which can be attributed to the stretching vibration of the uncharged dimer of carboxylic groups. The shoulder at 1630 cm$^{-1}$ might result from the short-range interactions of carbonyl dipoles or hydrogen bonding between more than two carboxylic groups. The peak at 1400 cm$^{-1}$ represents the symmetric stretch of –COO$^-$.$^2$ For the spectrum of PAA-dopamine, an amide peak appears at 1550 cm$^{-1}$, indicating dopamine was covalently conjugated onto PAA.$^3$ The peak at 1450 cm$^{-1}$ of PAA-dopamine is attributed to the aromatic C=C stretch.
Figure S2. (a) UV-vis spectra of PAA-dopamine/PAH multilayer film fabricated on quartz measured after the deposition of each bilayer. The insert shows the layer number dependence of absorbance at 280 nm. (b) Thickness of PAA-dopamine/PAH multilayer film on silicon slide as a function of number of bilayers measured by ellipsometry. Error bars indicate standard deviation (SD). The fit lines are to guide the eye.

Growth Pattern of PAA-dopamine/PAH Multilayer Film. As shown in Figure S2a, the absorbance at 280 nm, the characteristic peak of unoxidized catechol group, increases exponentially as a function of the assembly cycle. A similar exponential increase of film thickness from 2 nm to approximately 220 nm with the bilayers number from 1 to 9 (Figure S2b), is in well accordance with the result obtained by UV-visible spectroscopy.
**Figure S3.** (a) Full and (b) partial FTIR spectra of the (PAA-dopamine/PAH)$_9$ films before (black) and after (red) cross-linked.

**FTIR Spectra Support of the Multilayer Films Cross-linking.** As shown in Figure S3, although the FTIR spectra of the two films are similar at most scope, a striking divergence presents in the range from 830 to 880 cm$^{-1}$. For the uncross-linked film, the absorption peak at 843 cm$^{-1}$ is assigned to the out of the plane bending vibration of adjacent C-H of the phenol groups, while the peak at 860 cm$^{-1}$ is attributed to isolated C-H vibration of the aromatic groups.$^4$ After cross-linking, only one broad peak appeared around 845 cm$^{-1}$ that can be ascribed to the formation of catechol-amine via Michael addition and di-DOPA via dismutation (Scheme 1).
Figure S4. The mass residual of uncross-linked and cross-linked films after solution etching. The columns represent the films of untreated (black), treated with 0.1 M NaOH (red), 0.1 M HCl (green) and 5 M NaCl solution (blue). The etching time for uncross-linked and cross-linked film was 10 min and 2 h, respectively. The mass residual was calculated on the basis of the absorbance of the films at 280 nm from UV-visible spectra. The error bars indicate SD of five measurements.

Stability Comparison for Uncross-linked and Cross-linked Multilayer Films. As shown in Figure S4, the mass residuals of the uncross-linked films are less than 30% after 10 min acid, base or salt solution etching. The fast and great disassembly of the multilayer films is caused by the disruption of electrostatic force, which result from the protonation of acrylic acid unit in acidic solution, deprotonation of amine unit in basic solution or charge shielding effect in high concentration electrolyte solution. After cross-linking, however, the mass residuals are more than 94% even after 2 h etching, demonstrating the stability of the film is enhanced dramatically due to the chemical covalent bonding. We also tried to assess the film stability through measuring the film
thickness variation using ellipsometry. But the results were not satisfied because the uniform flat surface of the uncross-linked film turned to be greatly inhomogeneous after solution etching (As shown in Figure 4a, b, and c). It is hard to precisely determine and compare the thickness of films with a flat and microstructured morphology.
Figure S5. XPS spectrum of the cross-linked (PAA-dopamine/PAH)$_9$ film modified with 1-dodecanethiol.

Unsuccessful 1-Dodecanethiol Modification of a Firstly Cross-linked Multilayer Film. Figure S5 is the XPS spectrum of a cross-linked (PAA-dopamine/PAH)$_9$ film modified with 1-dodecanethiol. No sulfur characteristic peak (S$_{2p}$=168 eV) is observed, indicating the thiol did not grafted onto film surface. It is more likely that the catechol groups were consumed during oxidation cross-linking. Therefore, we proposed that modification with thiols should be performed before cross-linking.
Figure S6. (a and b) UV-visible spectra of (PAA-dopamine/PAH)$_9$ film before and after thiols modifications. (c and d) UV-visible spectra of thiols (c for 1-dodecanethiol and d for polyPEG-SH) modified (PAA-dopamine/PAH)$_9$ films after cross-linked and then solution etching.

Reactivity of Surface Modified Multilayer Films and Stability Tests after Cross-linking. As Shown in Figure S6 a and b, the UV-visible spectra of the films before and after thiols modification is almost the same. The exhibition of characteristic peak at 280 nm after thiols modification implies most of the catechol inside the films is remained. Figure S6 c and d show the UV-visible spectra of the thiols modified films after cross-linking and then immersed in etching solutions, respectively. The few mass loss after solution etching demonstrates that the residual catechol groups inside the
thiols-modified films effectively made the films cross-linked, which endows the favorable stability of the functionalized films.
Figure S7. AFM height images (5 µm×5 µm) of 1-dodecanethiol modified (PAA-dopamine/PAH)$_9$ films (a) before and after (c) cross-linking, and (b) polyPEGA-SH modified films (b) before and (d) after cross-linking. The insert is the corresponding static water contact angle images of the films.

The Influence of Cross-linking Treatment on Morphology and Wettability of Thiols Modified Multilayer Films. Figure S7 show the morphology of thiols modified multilayer films before and after cross-linking. All films show abundant nano-protuberances on surface. In comparison to the sole thiols modified films, the size nano-protuberances on cross-linked films is increased, which is similar to the non-thiols-modified films. The contact angle is 63±1° for 1-dodecanethiol modified films after cross-linking, while 9±1° for polyPEGA-SH modified films. There are no significant distinctions from the uncross-linked ones. These results indicate the surface properties of functional films are not perturbed during oxidative cross-linking.
References:


