

Supporting Information

Orthogonal Redox and Optical Stimuli Can Induce Independent Responses for Catechol-Chitosan Films

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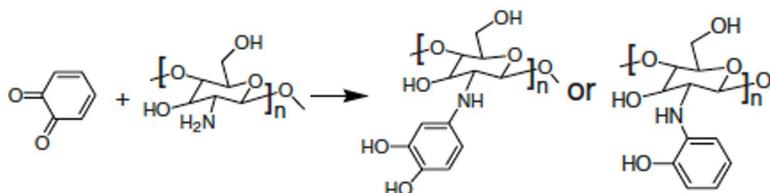
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The catechol films are fabricated through electrochemical grafting reactions. After the catechol is anodically oxidized at the electrode surface, the oxidation products (e.g., *o*-quinone) are reactive and can undergo grafting reactions with the amine of chitosan. As discussed in our previous reports,¹ the putative products of the grafting reactions might be formed through potential Schiff-base linkages and/or Michael-type adducts (**Fig. S1a**).

(a) Putative chemistry of (oxidized) catechol grafting reactions



(b) ATR-IR spectra of catechol region and control (c) Electrospray mass spectrum

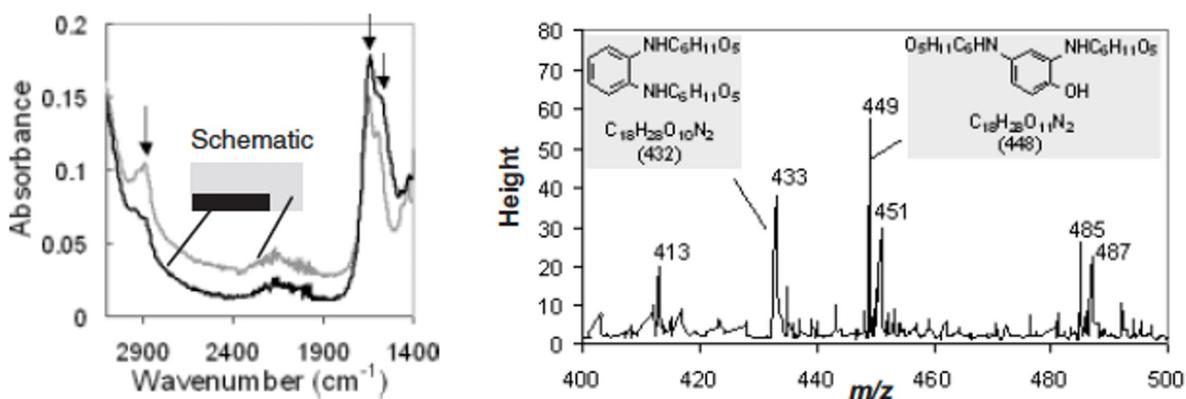


Fig. S1 Catechol's oxidative grafting to chitosan films and previously reported

characterizations.^{1,2} (a) Putative chemistry of catechol's electrochemical grafting reactions. (b) ATR-IR spectra of the catechol patterned region (black square) and un-patterned chitosan region. Reproduced from ref. 2 with permission from John Wiley & Sons, Copyright © 2005 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. (c) Electrospray mass spectrum for product solution formed during electrochemical reaction of catechol (0.2 M) and glucosamine (0.4 M)

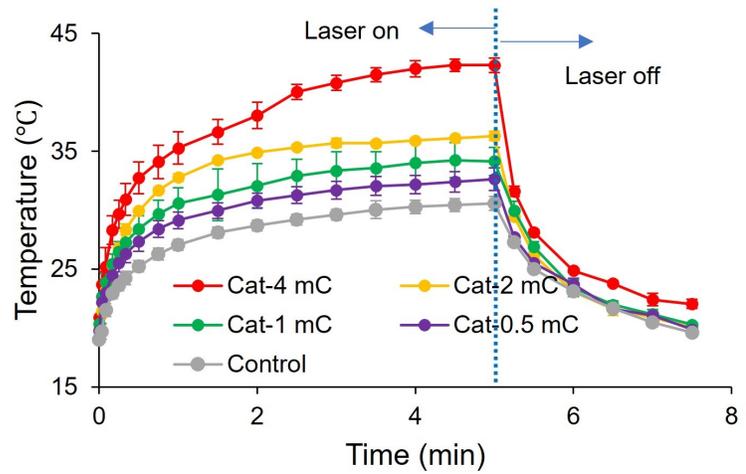
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This electrochemical grafting mechanism was supported by our previous chemical characterizations using attenuated total reflectance Fourier-transform infrared (ATR-FTIR) spectroscopy² and electrospray mass spectrometry¹. ATR-IR spectra show that (**Fig. S1b**), compared to the un-patterned chitosan region, the catechol patterned region has smaller absorbance in the regions for the stretching vibration of the protonated amine and amine at 2886 and 1593 cm^{-1} , which suggests that the oxidation products of catechol undergo covalent bond formation with amine group of chitosan.² For additional chemical evidence, electrospray mass spectrometry (**Fig. S1c**) was used to analyze the product formed through the reaction between electrochemically oxidized catechol and glucosamine (a monomeric unit of chitosan).¹ Two putative products are shown in **Fig. S1c** for peaks observed at m/z 433 and 449, and it suggests that the catechol films are probably formed through Schiff-base linkages and/or Michael-type adducts.¹

(a) Control hydrogel on glass slide



(b) Maximum temperatures of thermograms



(c) Thermograms after 5 minutes irradiation

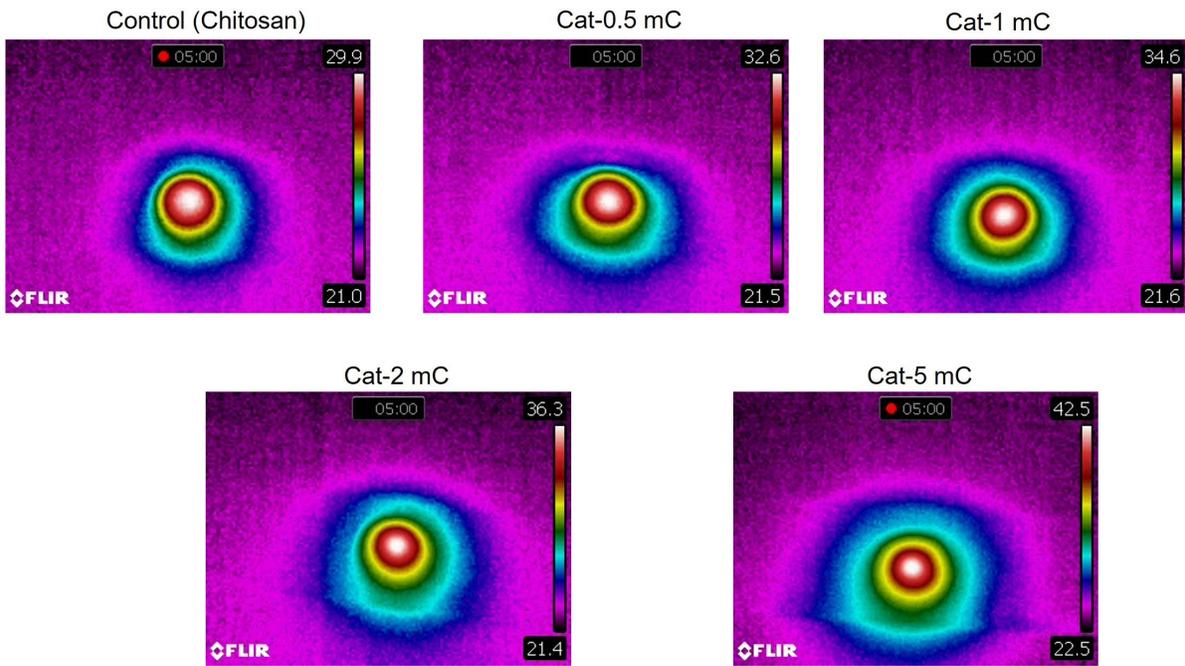


Fig. S2 Photothermal properties of patterned catechol films. (a) Optical image of hydrogel on a $\sim 150 \mu\text{m}$ thick glass slide. (b) The maximum temperatures of the patterned regions were recorded during and after irradiation (808 nm; 0.75 W/cm^2 ; data represent mean values \pm SD ($n=3$)). (c) Thermograms of the irradiated samples, temperature is in unit of $^{\circ}\text{C}$.

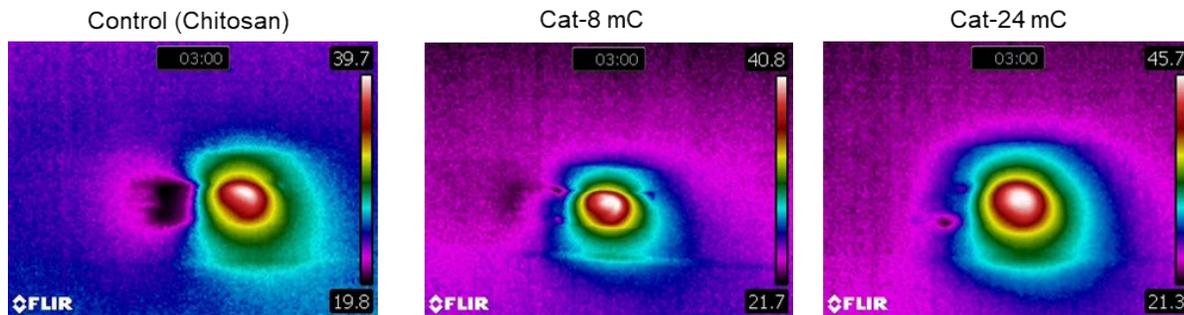


Fig. S3 Thermograms of catechol-chitosan coated electrodes after 3 minutes irradiation, temperature is in unit of °C.

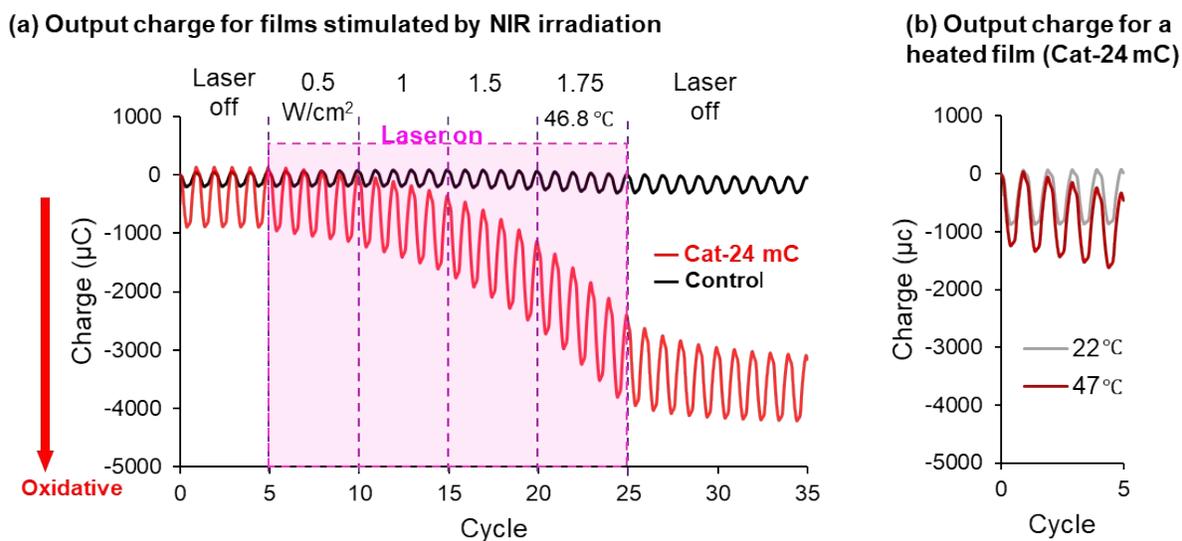


Fig. S4 (a) Times-series data of the output charge ($Q = \int i dt$) responses by integrating current output in **Fig. 3d**. Without irradiation, the output charge oscillates within each cycle without showing a net trend indicating that oxidation and reduction are balanced. With irradiation, there is a trend toward a net oxidative charge transfer. (b) When redox probing was performed at elevated temperature (47 °C) in the absence of irradiation (**Fig. 4b**), the output Q also has a trend toward net oxidative (vs. redox-probing at lower temperature). All measurements were

performed with an electrode coated with either a chitosan film (control) or a catechol (24 mC)-chitosan film.

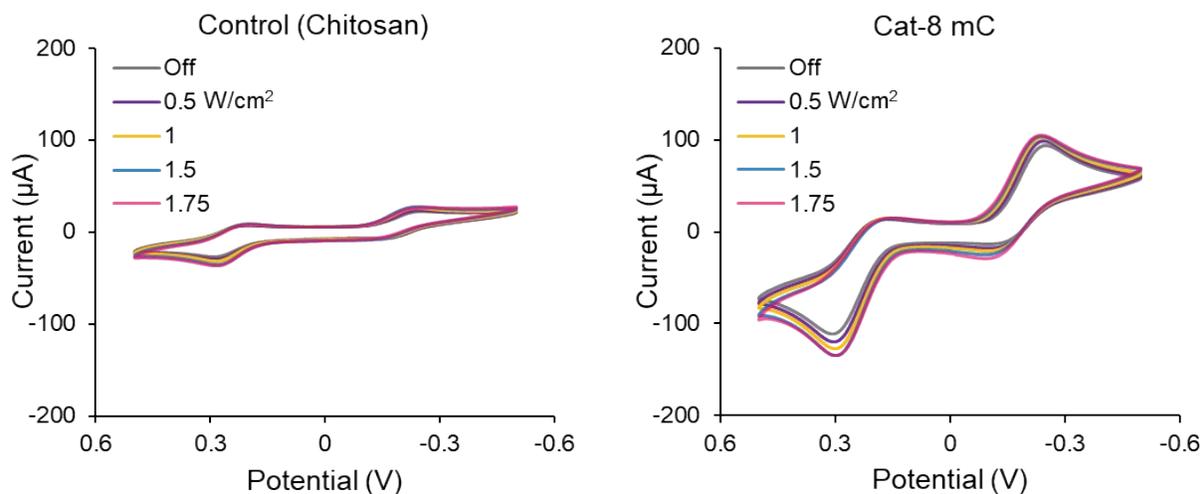


Fig. S5 Cyclic voltammograms of electrodes coated with either the control chitosan film or the catechol-chitosan (Cat-8 mC) film that were simultaneously stimulated by redox-probing and NIR-irradiation (808 nm). Solution: 1 mM $\text{Ru}(\text{NH}_3)_6\text{Cl}_3$ and 1 mM 1,1-Ferrocenedimethanol in 0.1 M phosphate buffer.

References

- (1) Wu, L.-Q.; McDermott, M. K.; Zhu, C.; Ghodssi, R.; Payne, G. F.; M. K., M.; C., Z.; R., G.; G. F., P. Mimicking Biological Phenol Reaction Cascades to Confer Mechanical Function. *Adv. Funct. Mater.* **2006**, *16* (15), 1967–1974. <https://doi.org/10.1002/adfm.200500792>.
- (2) Wu, L. Q.; Ghodssi, R.; Elabd, Y. A.; Payne, G. F. Biomimetic Pattern Transfer. *Adv. Funct. Mater.* **2005**, *15* (2), 189–195. <https://doi.org/10.1002/adfm.200400279>.