Supporting Information

Norepinephrine: Material-Independent, Multifunctional Surface Modification Reagent

Sung Min Kang,[†] Junsung Rho,[§] Insung S. Choi,[†] Phillip B. Messersmith,*[, §,‖]

Haeshin Lee,*[,†,‡]

[†]Department of Chemistry and [‡]Graduate School of Nanoscience & Technology, KAIST

Institute for BioCentury & NanoCentury, KAIST, 335 Science Rd. Daejeon 305-701, Korea,

[§]Biomedical Engineering Department, Northwestern University,

2145 Sheridan Rd. Evanston, IL 60208,

[‖]Materials Science and Engineering Department, Northwestern University,

2220 Campus Dr. Evanston, IL 60208

* To whom correspondence should be addressed.

Email: haeshin@kaist.ac.kr or philm@northwestern.edu

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Complete list of authors in ref 1b

Adams, D. M.; Brus, L.; Chidsey, C. E. D.; Creager, S.; Creutz, C.; Kagan, C. R.; Kamat, P. V.; Lieberman, M.; Lindsay, S.; Marcus, R. A.; Metzger, R. M.; Michel-Beyerle, M. E.; Miller, J. R.; Newton, M. D.; Rolison, D. R.; Sankey, O.; Schanze, K. S.; Yardley, J.; Zhu, X. *J. Phys. Chem. B* **2003**, *107*, 6668.

Complete list of authors in ref 4b

Mahdavi, A.; Ferreira, L.; Sundback, C.; Nichol, J. W.; Chan, E. P.; Carter, D. J. D.; Bettinger, C. J.; Patanavanich, S.; Chignozha, L.; Ben-Joseph, E.; Galakatos, A.; Pryor, H.; Pomerantseva, I.; Masiakos, P. T.; Faquin, W.; Zumbuehl, A.; Hong, S.; Borenstein, J.; Vacanti, J.; Langer, R.; Karp, J. M. *Proc. Natl. Acad. Sci. U.S.A.* **2008**, *105,* 2307.

Experimental details

1. Poly(norepinephrine) coating

Solid substrates were cleaned in acetone or ethanol with sonication prior to use. Poly(norepinephrine) coating was performed by immersing substrates in a buffer solution (2 mg of L-(-)-norepinephrine per milliliter of 10 mM Tris, pH 8.5) at room temperature. The coated substrates were rinsed with deionized water and methanol, and dried under a stream of argon.

2. Characterizations

XPS spectra were obtained using an Omicron ESCALAB (Omicron, Taunusstein, Germany) with a monochromatic Al Kα (1486.8 eV) 300-W X-ray source, a flood gun to counter charging effects, and ultrahigh vacuum (~10^{-9} torr). The takeoff angle was fixed at 45^{o} except as otherwise mentioned. IR spectra were obtained in single-reflection mode using a dry N_2-purged Thermo Nicolet Nexus FT-IR spectrophotometer equipped with the smart SAGA (smart apertured grazing angle) accessory. The *p*-polarized light was incident at 80° relative to the surface normal of the substrate, and a narrow band mercury-cadmium-telluride (MCT) detector cooled with liquid nitrogen was used to detect the reflected light. We averaged 2000 scans to yield the spectra at a resolution of 4 cm^{-1}. The thickness of poly(norepinephrine) layers and PCL films were measured with a Gaertner L116s ellipsometer (Gaertner Scientific Corporation, IL) equipped with a He-Ne laser (632.8 nm) at a 70° angle of incidence. A

refractive index of 1.46 was used for all the films. AFM imaging was performed in a tapping mode on a Nanoscope IIIa multimode scanning probe microscope (Veeco, United States) with a tapping mode etched silicon probe (TESP). Static water contact angle measurements were performed using a Phoenix 300 goniometer (Surface Electro Optics Co., Ltd., Korea).

3. Trypsin immobilization on the poly(norepinephrine) layer

Poly(norepinephrine)-coated silicon substrates (8 hrs coating) were rinsed with water and subsequently transferred to a trypsin solution (1.5 mg of trypsin per milliliter of 10 mM Tris buffer pH 8.5). After overnight conjugation reaction, the substrates were rinsed with water and then transferred to BAPNA (N-α-benzoyl-D,L-arginine *p*-nitroanilide) solution to measure the trypsin activity immobilized on the substrates. 3 mg/mL of BAPNA was dissolved in 50 mM Tris buffer pH 7.4 with 10 mM $CaCl_2$. The trypsin activity was monitored at 420 nm by UV-Vis spectrophotometer (HP8453, Agilent).

4. Ring-opening polymerization of ε-CL on the poly(norepinephrine) layer

Poly(norepinephrine)-coated Au substrate (1 hr coating) was rinsed with water and methanol several times and then dried under a stream of argon. The poly(norepinephrine)-coated substrate was placed in a reaction vessel and dried under vacuum at 55 ^{o}C for 24 hrs. After drying, the poly(norepinephrine)-coated substrate was treated with $Sn(Oct)_2$ (5 μL) in 5 mL

of anhydrous toluene for 1 hr at 55 ^{o}C. The monomer, ε-CL (0.5 mL), was then slowly added by syringe and the mixture was heated at 55 ^{o}C for 24 hrs. The PCL-coated substrate was taken, thoroughly washed with toluene, and sonicated for 5 min in 1,2-dichloroethane to remove physisorbed polymers. Prior to analysis, prepared substrate was further dried under vacuum at 55 ^{o}C for 24 hrs.

Figure S1. Suggested chemical structure of poly(norepinephrine).

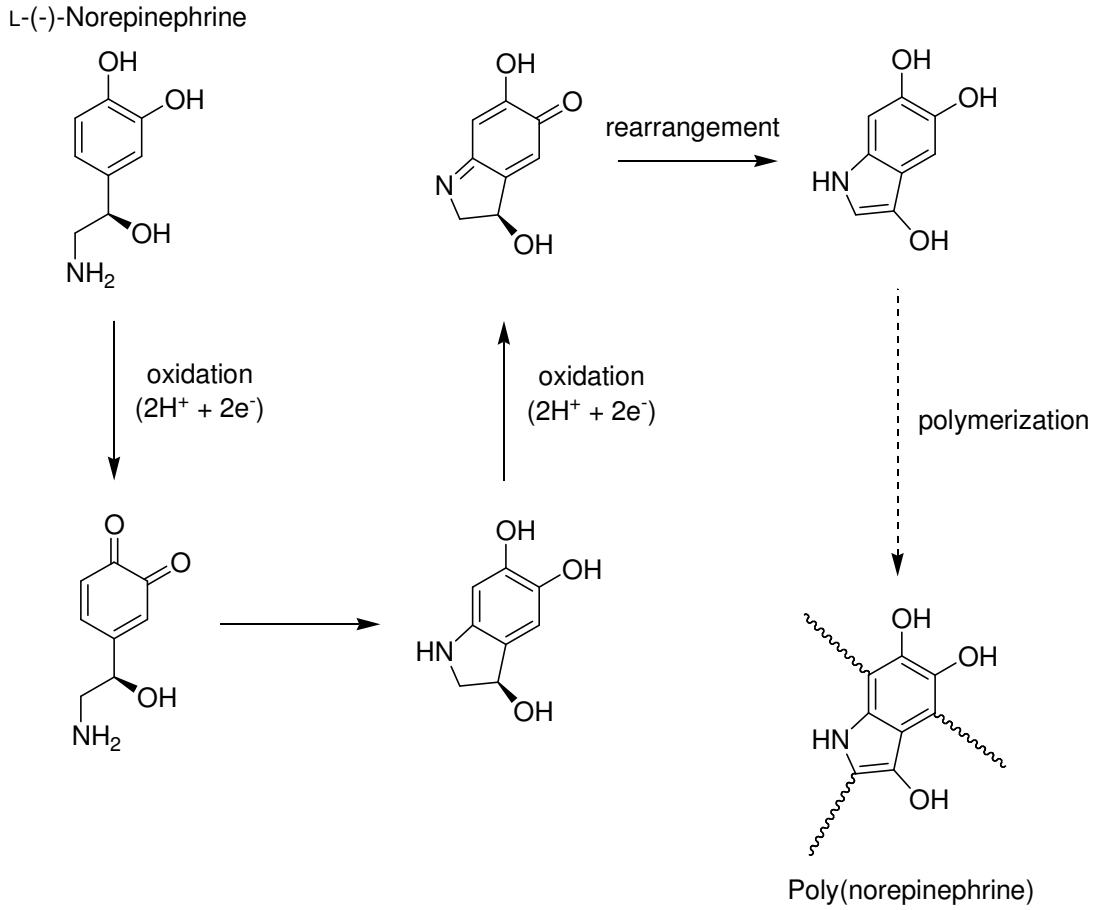

Figure S2. XPS spectra of TiO_2 before (left) and after (right) coating by poly(norepinephrine).

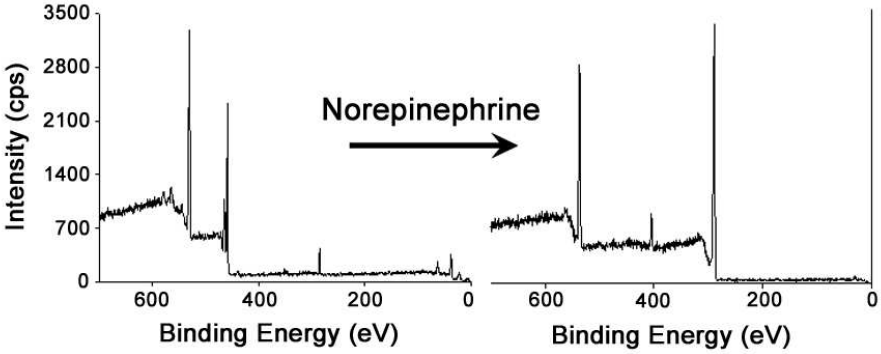

Figure S3. FT-IR spectra of (a) poly(norepinephrine)-coated and (b) PCL-coated substrate.

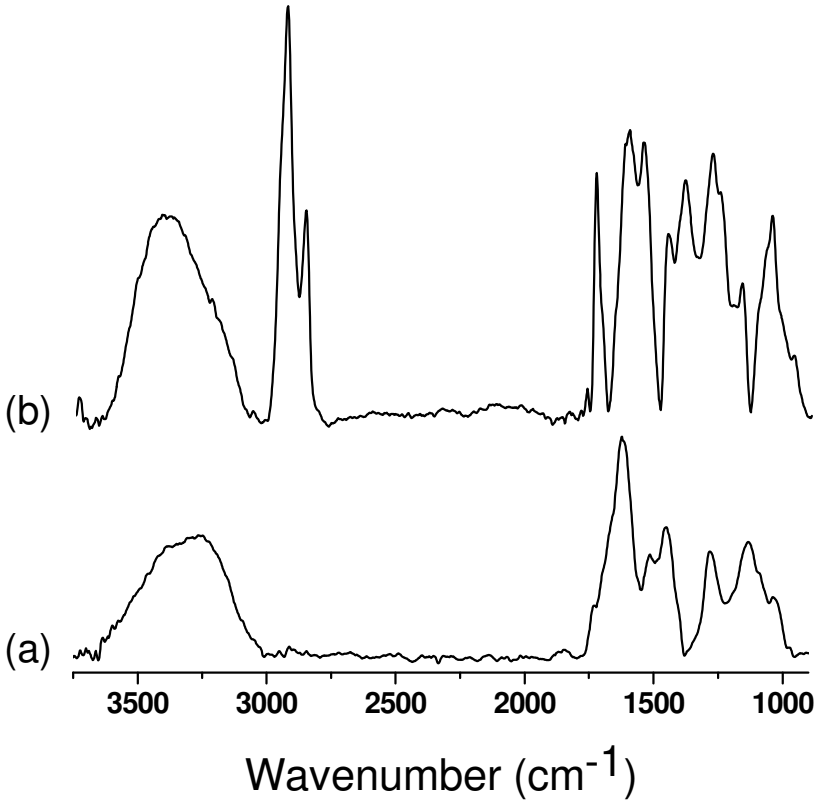

Figure S4. AFM images of (a) poly(norepinephrine)-coated and (b) PCL-coated substrate (The scale bar is equally applicable to both images.)