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Underwater Superoleophobic Surfaces Prepared from Polymer Zwitterion/Dopamine Composite Coatings

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Abstract

Hydration is central to mitigating surface fouling by oil and microorganisms. Immobilization of hydrophilic polymers on surfaces promotes retention of water and a reduction of direct interactions with potential foulants. While conventional surface modification techniques are surface-specific, mussel-inspired adhesives based on dopamine effectively coat many types of surfaces and thus hold potential as a universal solution to surface modification. Here, we describe a facile, one-step surface modification strategy that affords hydrophilic, and underwater superoleophobic, coatings by the simultaneous deposition of polydopamine (PDA) with

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Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

poly(methacryloyloxyethyl phosphorylcholine) (polyMPC). The resultant composite coating features enhanced hydrophilicity (i.e., water contact angle of $\sim 10^\circ$ in air) and antifouling performance relative to PDA coatings. PolyMPC affords control over coating thickness and surface roughness, and results in a nearly 10 fold reduction in *Escherichia coli* adhesion relative to unmodified glass. The substrate-independent nature of PDA coatings further promotes facile surface modification without tedious surface pretreatment, and offers a robust template for codepositing polyMPC to enhance biocompatibility, hydrophilicity and fouling resistance.

Graphical abstract

An antifouling composite coating is prepared by one-step simultaneous deposition of a polymer zwitterion with the surface-adherent polydopamine. The facile incorporation of poly(2-methacryloyloxyethyl phosphorylcholine) (polyMPC) into these coatings reduced bacteria *Escherichia coli* (*E. coli*) adhesion by nearly 10-fold relative to polydopamine and glass control samples

Keywords

dopamine; polydopamine; surface modification; zwitterionic polymer; superhydrophilic; phosphorylcholine

Introduction

Superhydrophilic surfaces that also exhibit underwater superoleophobicity are important for preventing biofouling, mitigating oil adhesion, reducing drag, and enabling oil-water separation.^[1–8] Such materials are characterized by very low water contact angles (CA) in air (i.e., 10°), and extreme oil repellency under water (CA > 150°). Controlling surface chemistry and morphology are crucial to achieving such extreme wetting properties. While surface functionalization provides a means to alter surface energy, roughness further influences wetting, described for example by Cassie.^[9] Oil droplets bead on a hydrophilic surface in water due to surface tension, and water associated with the surface comprises a

composite interface that minimizes surface-oil contact. Developing a novel, universal coating strategy that gives ultrathin (nominally 1–2 nm) hydrophilic coatings would dictate surface wettability, while retaining the desired composition and properties of the underlying substrate.

Polymer zwitterions (i.e., sulfobetaine, carboxybetaine and phosphorylcholine) are of growing interest as alternatives to neutral synthetic polymers, such as poly(ethylene glycol) (PEG) and poly(*N*-vinyl pyrrolidone) (PVP).^[10–18] Many polymer zwitterions are extremely water soluble and biocompatible, such that even a thin layer can effectively render a surface hydrophilic and antifouling.^[19] Immobilization of polymer zwitterions on surfaces has been achieved by surface-initiated polymerization,^[20–22] layer-by-layer assembly,^[23] and solution casting.^[17,24–25] However, most examples are substrate-specific and require surface pre-treatment to promote polymer adhesion. Inspired by mussel adhesive proteins that enable robust adhesion to numerous substrates, surface modification with dopamine and other catecholamine derivatives is developing into a more universal surface modification platform.^[26–36] Catechol-containing structures are thought to undergo oxidative polymerization under basic conditions on surfaces, while the reactivity of polydopamine (PDA) towards nucleophiles facilitates its use as a primer layer for immobilization of amine or thiol functionalized ad-layers.^[37–40]

Messersmith and others have reported catechol-containing surface initiators for controlled radical polymerization of sulfobetaine methacrylate, affording surfaces that are resistant to protein and cell adhesion.^[21,41–42] Alternatively, fixing catechols to polymer chain-ends enables facile modification of silica, gold and metal oxides in the ‘grafting to’ approach.^[43–44] However, depositing catechol-containing hydrophilic polymers onto hydrophobic surfaces remains challenging. In one recent example, Jiang and coworkers employed catechol-terminated poly(carboxybetaine methacrylate)s and dopamine to modify hydrophobic surfaces, utilizing catechol chain-ends in PDA polymerization, resulting in PDA-poly(carboxybetaine methacrylate) composite coatings that reduced protein fouling.^[45]

In complementary approaches, non-covalent interactions provide a simple and efficient approach to functional surfaces and hybrid materials.^[46–47] PDA can participate in hydrogen bonding, exploited for example by Städler in the simultaneous codeposition of PDA and nonionic polymers including PEG, poly(vinyl alcohol) and poly(*N*-isopropylacrylamide) (PNIPAM) on silicon (Si) wafers.^[48] The hydrogen bonding capabilities of poly(methacryloyloxyethyl phosphorylcholine) (polyMPC)^[18] led us to examine the impact of polyMPC on PDA formation and PDA-polyMPC composite coatings. Here we describe the simultaneous codeposition of polyMPC and dopamine as a one-step, facile method to construct superhydrophilic, antifouling PDA-polyMPC composite coatings on a variety of surfaces including Si, glass, polystyrene, and perfluorinated Si. Deposition kinetics, surface roughness, surface composition and coating stability were characterized by ellipsometry, atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared (FT-IR) spectroscopy. Surfaces coated with PDA-polyMPC provided a statistically significant reduction in *Escherichia coli* (*E. coli*) attachment relative to glass. We note that during the course of our work, Xu and coworkers reported the simultaneous deposition of poly(sulfobetaine methacrylate) and dopamine on polypropylene.^[8]

Results and Discussion

To evaluate the effect of polyMPC on PDA film formation, Si wafers were immersed in a dopamine solution (2 mg/mL in 10 mM Tris buffer solution, pH 8.5) containing different amounts (0–5 mg/mL) of polyMPC ($M_n = 15.3$ kDa, $\text{MW} = 1.2$) for a predetermined time (Figure 1a). Experiments were conducted in 12-well cell culture plates under ambient conditions, open to air, with continuous agitation using an orbital shaker at 400 rpm. The substrates were rinsed with deionized water, dried and characterized by ellipsometry. Figure 1b shows the kinetics of PDA-polyMPC growth on Si wafers as a function of polymer concentrations. Coating thickness increased linearly with respect to immersion time, and plateaued at $t = 4$ h (Figure S1). For example, a 2 mg/mL dopamine solution without polyMPC yielded 28.9 ± 0.5 nm thick coatings after an immersion time of 4 h; over the same time-frame, a 1 mg/mL polyMPC solution caused little change in film thickness. PolyMPC concentrations of 2, 3.5, and 5 mg/mL led to coatings having thicknesses of 20.8 ± 2.1 , 13.5 ± 0.6 nm, and 10.1 ± 0.6 nm. Coating thickness was reduced further, to 5 nm, using 10 mg/mL polyMPC solutions. When the polyMPC concentration was kept constant at 2 mg/mL, the coating thickness increased with dopamine concentration. Ellipsometry determined that PDA-polyMPC coatings with dopamine concentrations of 0.5 and 1 mg/mL had thicknesses of 3.3 ± 0.1 and 16.4 ± 0.6 nm, respectively. Coating thickness showed no dependence on polyMPC molecular weight (Table S1). The brown color of the PDA-coated surfaces results from its melanin-like structure and is indicative of successful PDA deposition. PDA and PDA-polyMPC-coated glass slides were characterized by transmission mode UV-vis spectroscopy to evaluate the influence of polyMPC incorporation on coating transmittance. The coating thickness on glass was approximated by measuring the coating thickness on Si wafers immersed in the same coating solution. Ellipsometry measurements on surfaces modified with 2 mg/mL dopamine revealed 39 ± 3 nm coatings after 6 h, and reduced thickness, to 26 ± 1 nm and 12 ± 1 nm, from solutions containing 2 and 5 mg/mL polyMPC, respectively. UV-Vis spectroscopy confirmed >80% visible light transmission through PDA-polyMPC coated glass slides (Figure S2); indeed, PDA-polyMPC coated samples are more transparent than PDA coated glass at comparable coating thickness.

Characterization of Modified Surfaces: Morphology, Composition and Wettability

The surface morphology of PDA-polyMPC composite coatings on Si wafers was characterized by atomic force microscopy (AFM) (Figures 2a–f). The roughly spherical features observed by AFM represent agglomerated PDA expected to result from oxidative polymerization of dopamine. Aggregate size is sensitive to dopamine concentration, pH, temperature, and selection of buffer and additives.^[49–52] The observation of these aggregate morphologies is consistent with previous reports (Figure 2g and Figure S3) of root mean square roughness (R_{rms}) of PDA coatings (determined by AFM) determined by ellipsometry.^[36,49,53] The PDA-polyMPC aggregates formed in the presence of 5 mg/mL polyMPC were smaller than those obtained using 2 mg/mL polyMPC, resulting in a smoother surface-adherent coating. Roughness varied with concentration: in the formation of 10 nm PDA-polyMPC films, use of 2 mg/mL polyMPC solution produced R_{rms} value of 10.8 nm, while the 5 mg/mL polyMPC solution yielded a R_{rms} value of 5.8 nm. Unlike pure PDA coatings, no visible precipitate was observed during PDA-polyMPC codeposition;

instead, stably-suspended aggregates were isolated by centrifugation. Transmission electron microscopy (TEM) revealed smaller aggregates with increasing polyMPC concentration, in agreement with the fact that PDA-polyMPC coatings had a smoother surface morphology than the pure PDA coatings as characterized by AFM (Figure 2h–j). Such a size reduction of PDA aggregates in the presence of a hydrophilic polymer agrees with light scattering results of Jiang and coworkers, in which catechol-terminated poly(carboxybetaine methacrylate) reduced PDA aggregate size from 3 microns to < 100 nm.^[45]

The elemental compositions of PDA and composite polyMPC coatings were probed by XPS, with representative spectra presented in Figure 3. Successful incorporation of polyMPC was confirmed by the characteristic phosphorus P_{2p} signal at 132.7 eV, which is absent in pure PDA coatings. Moreover, a broader C_{1s} peak arising from the carbonyls and a quaternary ammonium N_{1s} peak at 402.1 eV, unique to PC groups, was observed in the PDA-polyMPC composite coatings. High resolution XPS gave a phosphorus-to-carbon (P/C) ratio of 0.024 (~ 3.8 dopamines per PC group). The P/C ratio of samples prepared under identical conditions varied from 0.022 to 0.027, corresponding to 3.3–4.3 dopamine molecules for every PC group, even at larger penetration depths achieved with angle-resolved measurements.

The observed incorporation of polyMPC into PDA coatings is presumably promoted by interactions between residual catechol and phosphorylcholine. The FT-IR spectra in Figure 3e confirmed the presence of polyMPC in the composite coatings. Characteristic polyMPC absorption includes C=O stretching vibrations at 1720 cm^{-1} , C-O and P-O signals at 1082 cm^{-1} , and $-N^+(CH_3)_3$ at 971 cm^{-1} ; PDA C=C stretches and N-H bending vibrations are evident at 1604 and 1608 cm^{-1} . The P-O-C deformation vibration of polyMPC at 1482 cm^{-1} shifted to 1492 cm^{-1} in the coating, and new vibronic stretching peaks at 1224 and 1199 cm^{-1} were assigned to the phenolic C-O and P=O groups, respectively.^[54–56] Importantly, these polyMPC signals remained even after extensive rinsing with water.

Coating Stability

The stability of PDA-polyMPC composite coatings on Si wafers was evaluated against aqueous solutions with pH values of 1, 4, 7 and 10 for 24 h and 7 days. PDA-polyMPC composite coatings showed good stability from pH 4 to 10, with >80% of coating thickness retained after 7 days (determined by ellipsometry) (Figure 4a). XPS revealed phosphorus and quaternary ammonium groups with P/C ratios remaining in the 0.020–0.025 range after incubation at pH 4–7 for 7 days, similar to the as-prepared PDA-polyMPC modified substrates. PDA and PDA-polyMPC coating thicknesses decreased by 30–40% after incubation at pH 1 for 7 days, and by 19–24% after 7 days when placed in 0.1M NaCl. However, despite this reduction in coating thickness, the substrates retained low water CA values in air ($11 \pm 3^\circ$) suggesting a good retention of polyMPC within the composite coatings. To improve coating stability, PDA and PDA-polyMPC coated wafers were oxidatively crosslinked^[57–58] by immersion in aqueous sodium periodate (5 mM) for 12 h. Following this treatment, both PDA and PDA-polyMPC coatings remained intact after 7 days (Figure 4b), and exhibit essentially no thickness reduction even at pH 1 and in 0.1M $NaCl_{(aq)}$. Partial coating deterioration was observed only after sonicating the coated

substrates in water at 35 kHz. For example, a 29 nm PDA coating decreased to 23 nm after 60 min sonication, while a PDA-polyMPC coating with an initial thickness of 26 nm decreased to 20, 17.5, and 12 nm after 15, 30, and 60 min sonication. Thus, the PDA-polyMPC composite coatings are less stable under these conditions than pristine PDA coatings. XPS spectra (Figure S4) revealed a loss of polymer coverage as indicated by more intense Si signals from the underlying substrate after longer sonication time. Nonetheless, even under harsh conditions, including sonication, the P_{2p} signal remains, confirming the presence of polyMPC throughout the composite coatings.

The wetting behavior of PDA and PDA-polyMPC modified Si wafers was studied in air, and under water, by sessile drop CA measurements. PDA and PDA-polyMPC modified Si wafers exhibited static water CAs of $46 \pm 2^\circ$ and $13 \pm 0.5^\circ$ (Figure 5a–b), respectively. Underwater, a PDA coated Si wafer had a chloroform CA of $148 \pm 3^\circ$, while a PDA-polyMPC coated Si wafer had a CA of $157 \pm 2^\circ$, well into the superoleophobic range.^[5,59] The CA sample stage was inclined at a 2° angle to investigate the impact of surface chemistry on oil transport and adhesion properties, using chloroform as the probe oil. Photographs of oil droplets rolling off the coated surfaces are shown in Figures 5d and 5e. For PDA, an oil (5 μ L, chloroform) droplet remained spherical in shape upon contacting the PDA-coated surface over the first few seconds; the drop rolled down the inclined plane, then became pinned to the surface after 5 s, and it remained pinned even at a tilt angle of 60° (Figure 5c). This phenomenon is presumably caused by depletion of water at the liquid-solid interface, leading to direct contact of oil with the polymer coating. Similar droplet behavior was observed on an unmodified silicon wafer. In contrast, immediately upon tilting the PDA-polyMPC coated Si wafer, the droplet slid away. The enhanced hydrophilicity of PDA-polyMPC coating minimizes contact between the oil and substrate, allowing facile rolling of the droplet, a result that is strongly encouraging for using polyMPC-PDA coatings in applications where mitigating oil fouling is crucial.

The debate over the mechanism of PDA formation and its detailed structure notwithstanding,^[49,53,60–64] the incorporation of polyMPC into PDA films during the deposition process proved surprisingly simple. PDA-polyMPC coatings likely benefit from non-covalent interactions, as judged by reports on PDA interactions with cations, liposomes, and polymers containing hydrogen bonding capacity.^[48,65–67] Hydrogen bonding between phenols and phospholipids is documented, with the phenols serving as hydrogen bond donors and the phosphates as hydrogen bond acceptors.^[68–74] The PDA-polyMPC composites we describe could undergo: 1) phenol-phospholipid hydrogen bonding (the phenols serving as donors and phosphates as acceptors, and 2) cation- π interactions between the quaternary ammoniums and the aromatic PDA character.^[75] Notably, control experiments using only MPC monomer as the additive, rather than polyMPC, did not change the coating properties relative to PDA alone, highlighting the crucial role of polymeric multivalency for promoting robust interactions. We note that dip coating a PDA-coated substrate into a 2 mg/mL buffered solution (pH = 8.5) of polyMPC for 2 h yielded a coating showing a similar FT-IR spectrum and water contact angle ($10\sim13^\circ$) in air to that of PDA-polyMPC even after extensive rinsing with water. This result suggests good polyMPC adhesion to surfaces pre-modified with PDA. XPS analysis gave a P/C ratio of 0.08, which is close to the theoretical polyMPC composition. On the contrary, coatings obtained after dip-

coating with a solution of PEG or MPC monomer did not decrease water CA values. This PDA-polyMPC composite coating strategy proved versatile, and it was applied successfully to perfluorinated Si wafers (i.e., having a fluorocarbon monolayer). These coated surfaces exhibited a dramatic reduction in CA following PDA-polyMPC coating, from 108° to 11° (Table S2). This simple coating method precludes the need for surface-initiated polymer brush growth,^[46–47,55] and it is anticipated to be highly versatile across a variety of substrate compositions.

Bacterial Adhesion

PDA and PDA-polyMPC coated glass slides were evaluated for their ability to resist the adhesion of the Gram-negative microorganism *E. coli*. Samples were incubated for shorter (2 h) and longer (24 h) time periods with 1.0×10^8 cells/mL suspensions of *E. coli* expressing green fluorescent protein (GFP). As shown in Figure 6, both PDA and PDA-polyMPC coated surfaces, after 2 h incubation, showed significantly lower bacteria attachment relative to the glass control. *E. coli* attachment was reduced by 65% for PDA modified surfaces, and 87% for PDA-polyMPC coated surfaces. While surfaces modified with PDA only exhibited short-term resistance against *E. coli* adhesion, significant bacterial fouling was seen after 24 h exposure, consistent with literature reports.^[38,76] Additional reports showed PDA-modified membranes to cause a 75% reduction in *Pseudomonas aeruginosa* biofouling over a 2 h period; nonetheless, significant fouling was observed over longer time frames when using non-disinfected bacteria-containing water.^[77–78] In our case, *E. coli* attachment was not reduced by a statistically significant amount (~13% for PDA-coated surfaces relative to the glass control after 24 h). However, PDA-polyMPC modified surfaces exhibited large reductions, >85%, in *E. coli* attachment relative to PDA-modified surfaces and glass controls, a remarkable improvement in bacterial fouling resistance.

The enhancement in antifouling properties is due to an enhancement in surface hydration, which is anticipated to reduce non-specific adsorption of proteins secreted by bacteria, thus providing longer-term anti-fouling properties than seen with PDA-only coated surfaces. This effect presumably renders PDA-polyMPC coated surfaces too 'slippery' for *E. coli* adherence. Of the few reports on polyMPC resistance to bacterial fouling, Ishihara and coworkers noted a large reduction in *E. coli* attachment on polyMPC grafted poly(ether ether ketone) after 1 h, though longer incubation times give more comprehensive data.^[79] Significantly, the PDA-polyMPC coating maintained its effectiveness against *E. coli* adhesion even after 24 h incubation, thus opening opportunities for this composite coating approach in practical applications and systems.

In summary, we report a codeposition method that, in one step, affords superhydrophilic surfaces using dopamine and polyMPC, thus leveraging non-covalent interactions between catechol containing polymers and PC groups. Fine-tuning of coating thickness and roughness was achieved by adjusting polymer concentration and coating time. Codeposited PDA-polyMPC composite coatings were stable in pH 4 to 10 solutions, and they exhibited even greater pH and salt stability following oxidative crosslinking. The enhanced hydrophilicity offered by polyMPC produces underwater oil repellency, reflected in a chloroform CA of >150° for the composite coating. The PDA-polyMPC composite coatings

are much more hydrophilic than PDA coatings, and thus less prone to bacterial fouling, exhibiting a nearly 10 fold reduction in *E. coli* attachment relative to PDA-coated surfaces after 24 h, whereas PDA-coated surfaces exhibited significant bacterial fouling that was statistically equivalent to the glass control. The substrate-independent nature of the PDA coating enables facile surface modification without tedious surface pretreatment, and offers a robust template for codeposition of polyMPC to enhance biocompatibility, hydrophilicity and fouling resistance.

4. Experimental Section

Materials

4,4'-azobis(4-cyanovaleric acid) (97%), 2,2'-azobis(2methylpropionitrile), 4-cyano-4-(phenylcarbonothioylthio)pentanoic acid (>97%), dopamine hydrochloride (98%), 2-methacryloyloxyethyl phosphorylcholine (97%), sodium periodate tris(hydroxymethyl)aminomethane (Tris), tris(hydroxymethyl)aminomethane hydrochloride were purchased from Sigma-Aldrich and used as received. Poly(2-methacryloyloxyethyl phosphorylcholine) was synthesized using a modified literature procedure with methanol as the alternative solvent to water.^[80]

Characterization

Coating thickness measurements were performed using a Gaertner LSE stokes ellipsometer equipped with a 632.8 nm HeNe Laser at a fixed incidence angle of 70° with GEMP software. The refractive index (n) of PDA-and PDA-polyMPC composite coating was assumed to be 1.55.^[81] n=1.46 was used for the silica layer on Si wafers. Atomic force microscopy (AFM) was performed on a Digital Instruments Nanoscope III in tapping mode under ambient conditions using silicon cantilevers (spring constant 0.58 N/m). The static contact angles of water droplet (0.4 µL) in air or chloroform droplet (5 µL) underwater was measured by sessile drop method using a VCA Optima surface goniometer equipped with an automated pipetting system. Average CA and standard deviations were obtained from 5 measurements with 0.4µL for water and 5µL for chloroform. X-ray photoelectron spectra were acquired using a Physical Electronics Quantum 2000 Microprobe instrument with a monochromatic Al 50-W X-ray source under ultrahigh vacuum, and a 200µm spot area. The take off angle was fixed at 45°. High resolution scans were acquired to obtain chemical composition. Fourier-transform infrared (FT-IR) spectra were recorded on a PerkinElmer Spectrum 100 spectrometer with an ATR accessory or a Nicolet 6700 FT-IR spectrometer equipped with a Harrick VariGATR™ grazing angle accessory. UV-vis spectra were recorded on a PerkinElmer Lambda 25 UV/vis spectrometer. ¹H NMR spectra were recorded on a Bruker DPX300 spectrometer operating at 300MHz. Chemical shifts were calibrated to residual solvent signals. Aqueous gel permeation chromatography (GPC) was carried out at 25°C using 0.1 M sodium nitrate and 0.02 wt % sodium azide as eluent at a flow rate of 1.0 mL/min with an HP series 1050 pump, an HP 1047A refractive index detector, and three Waters Ultrahydrogel columns (7.8 × 300 mm) calibrated against poly(ethylene oxide) standards.

General Surface Modification Protocol

Si wafer coupons ($1 \times 1 \text{ cm}^2$) were cleaned by sequential sonication in acetone, water, isopropanol for 15 min followed by oxygen plasma treatment for 20 min. The cleaned coupons were then immersed in a solution of dopamine hydrochloride (2 mg/mL) containing variable amount of polyMPC (0–10 mg/mL) in 10 mM TRIS (pH 8.5) for a predetermined time at room temperature. The samples were placed in a 12-well cell culture well plate, containing 1 mL of freshly prepared coating solution in each well (well area = 3.8 cm^2), and placed on an orbital shaker (Aapptec Labmate™) set at 400 rpm. The coated samples were then gently rinsed with water and dried under nitrogen for further analysis by IR, XPS and ellipsometry.

Stability Evaluation

PDA and PDA-polyMPC coated Si wafers were placed in polystyrene 12-well cell culture plates (Falcon) and immersed in various aqueous solutions: pH 1, 4, 7, 10 and 0.1M NaCl for 24 h and 7 days. The treated wafers were rinsed with water and dried under a stream of nitrogen. The change in coating thickness was monitored by ellipsometry. Sonication was performed using a VWR Symphony ultrasonic cleaner operating at 48W/35kHz (Model No. 97043–988).

Oxidation of polydopamine to increase robustness

PDA and PDA-polyMPC coated Si wafers were placed in a 12-well cell culture plate and immersed in 1 mL of 5 mM NaIO_4 for 12 h. The samples were thoroughly rinsed with water and dried under a stream of nitrogen.

Bacterial Attachment

The static bacterial adhesion property of pristine glass, PDA (2 mg/mL dopamine) modified glass, and PDA-polyMPC (2 mg/mL dopamine and 5 mg/mL polyMPC) modified glass was evaluated using the model bacteria *E. coli* K12 (MG1655, expressing green fluorescent proteins). *E. coli* was cultured overnight in Luria-Bertani broth, washed and resuspended in M9 media to a final concentration of 1.00×10^8 cells/mL. Samples were placed at the base of separate wells in 6-well polystyrene plates (Fisher Scientific) and inoculated with 5 mL of *E. coli* suspension in M9 media. Following a 2 or 24 h incubation at 37°C , the growth media was removed via sterilized glass pipette and samples were lightly shaken and rinsed repeatedly with sterile PBS before analysis. Samples incubated for 2 h were fixed in fresh 4% paraformaldehyde for 10 min. A UV-sterilized coverslip was placed on top of the fixed samples and sealed with VALAP (equal parts Vaseline, lanoline, and paraffin wax) to provide a clean surface. Bacterial attachment was then quantified using a $60\times$ oil immersion objective (Nikon NF) on a Nikon-D Eclipse Confocal Microscope. Samples incubated for 24 h were analyzed using $50\times$ objective on a Zeiss Microscope Axio Imager A2M. Attachment (%) was quantified by analyzing 10–15 randomly acquired images over 3 parallel replicates using Image J 1.45 software (National Institutes of Health, Bethesda, MD). Statistical significance was accepted at $p < 0.001$ level.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Figure 1.

(a) Schematic illustration of PDA-polyMPC composite coatings and potential interpolymer interactions; (b) coating thicknesses obtained from 0.5 to 4 hours using a 2 mg/mL dopamine concentration and variable polyMPC concentration.

Figure 2.

AFM height images of (a–c) PDA-polyMPC coated Si wafers (2 mg/mL dopamine, 2 mg/mL polyMPC); (d–f) PDA-polyMPC coated Si wafers (2 mg/mL dopamine and 5 mg/mL polyMPC) as a function of incubation time; (g) PDA coated Si wafer (2 mg/mL dopamine, incubation time = 1 h). Scale bars for a–g = 1 μm; TEM images of aggregates isolated from (h) PDA coating solution with 2 mg/mL dopamine, (i) PDA-polyMPC coating solution with 2 mg/mL polyMPC and 2 mg/mL dopamine, and (j) PDA-polyMPC coating solution with 5 mg/mL polyMPC and 2 mg/mL dopamine. Scale bars for h–j = 100 nm.

Figure 3.

XPS spectra of PDA-polyMPC coated Si wafer: (a) survey scan, and (b–d) high-resolution C1s, N1s, P2p narrow scans as a function of electron binding energy; FT-IR spectra of (e) polyMPC, PDA and PDA-polyMPC coated Si wafers.

Figure 4. Thickness measurements of (a) PDA-polyMPC coated Si; and (b) sodium periodate (5 mM, 12 hours) oxidized PDA-polyMPC coated Si.

Figure 5. Photographs of static water contact angle measurement in air: (a) PDA-coated Si and (b) PDA-polyMPC coated Si wafer; (c) Pinning of chloroform on PDA-coated Si; Photographs of oil (chloroform) adhesion study with a stage tilt angle of 2° on (d) PDA coated Si wafer and (e) PDA-polyMPC coated Si wafer.

Figure 6.

Micrographs of *E. coli* incubated for 2 h on (a) glass control; (b) PDA (2 mg/mL dopamine)-coated glass, and (c) PDA-polyMPC (2 mg/mL dopamine and 5 mg/mL polyMPC)-coated glass. Normalized *E. coli* attachment after (d) 2 h and (e) 24 h on unmodified glass control, PDA and PDA-polyMPC modified glass slides. Values were normalized to percent coverage on the unmodified glass control. Statistical significance was evaluated by one-way ANOVA and the Bonferroni post-test. */** denotes statistically significant p value of 0.001 with respect to unmodified glass and PDA modified glass, respectively.