

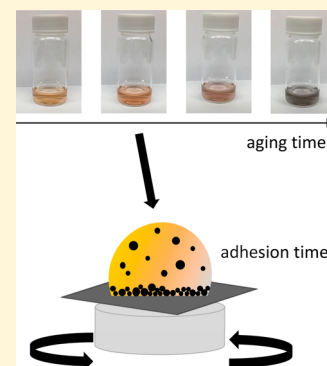
Using A Spin-Coater to Capture Adhesive Species during Polydopamine Thin-Film Fabrication

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Supporting Information

ABSTRACT: Spin-coating was evaluated as a technique to study events that occur during polydopamine (PDA) thin-film formation. The reaction variants studied included type of oxidant, dopamine (DA) concentration, pH, adhesion time prior to spin, substrate chemistry, and notably, DA solution aging time. A strong oxidant, sodium periodate (SP), and a weak oxidant, atmospheric oxygen were chosen. It was found that reactions in solution were much faster and produced much thicker PDA films with SP than with oxygen. PDA thickness correlated positively with DA concentration, SP solution pH, and adhesion time. DA oxidation and aggregation is a dynamic process, which is reflected in the DA aging-time parameter. PDA film thickness reached a maximum value as DA solution aged. Color photography, UV–vis spectroscopy, and dynamic light scattering indicated that the optimal DA aging time for PDA adhesion is the result of the evolution of PDA particle size and chemistry over time. The capture of the optimal aging-time window was identified as the critical parameter for preparing PDA films with continuity and appreciable thickness. When these conditions were applied in a modified dip-coating method, comparable PDA films were fabricated as those obtained from spin-coating. Native silicon wafers (SiO₂) as well as wafers that were modified with polydimethylsiloxane (PDMS) and amine-containing polydimethylsiloxane (PADMS) were chosen to represent a wide range of substrates with different substrate–PDA interactions. The main effect of substrate structural difference was on PDA film morphology. “Island” morphologies were obtained on PDMS where only hydrophobic interactions are responsible for PDA adhesion, while “speck” morphologies were observed on SiO₂ and PADMS. The stabilities of the fabricated PDA films were tested in 0.1 M HCl and DMSO. The SP-derived PDA films exhibited very little mass loss compared to those fabricated using either the conventional dip-coating method or oxygen as an oxidant. Choosing a strong oxidant, understanding the DA reaction dynamics, and taking advantage of the optimal DA aging time are important in the fabrication of stable PDA films on a variety of substrates.



■ INTRODUCTION

There has been growing interest in dopamine adhesion since the pioneering work by Lee and Messersmith in 2007.¹ Inspired by mussel adhesion, dopamine was chosen for its catechol and amine moieties that are key components in mussel foot proteins. The far-reaching appeals of dopamine adhesion lie in that dopamine can adhere to any substrate, function as a primer for other coating materials, and co-deposit with other functional molecules. Due to its universal adhesiveness and ease of manipulation, dopamine has a wide range of applications in biomedical and environmental sciences, as well as in industrial and consumer sectors. There are excellent reviews of the current state of research and development in the field.^{2–7}

The dopamine oxidation–aggregation mechanism has been an active focus of research. It is now accepted that dopamine (DA) undergoes oxidation to form dopaminequinone (DQ), followed by cyclization and oxidation to form dopamine-chrome (DC) and 5,6-dihydroxyindole (DHI) (Scheme 1).^{8,9} Even though acid (H⁺) is one of the oxidation products, it is consumed in the half reaction involving the oxidant. Thus, only

kinetics, not thermodynamics, are dependent on pH for the overall redox reaction.¹⁰ However, another study reports that different reaction products are obtained at different pH values and that solution pH decreased significantly as reaction progressed.¹¹ DA and the various oxidized species form aggregates,^{12–14} which are referred to as polydopamine (PDA). There are a myriad of interactions responsible for PDA formation, including noncovalent interactions—hydrophobic, π -cation, π - π stacking, hydrogen bonding, and electrostatic and covalent bonds.¹² The chemical natures and physical structures of PDA particles, however, remain elusive.

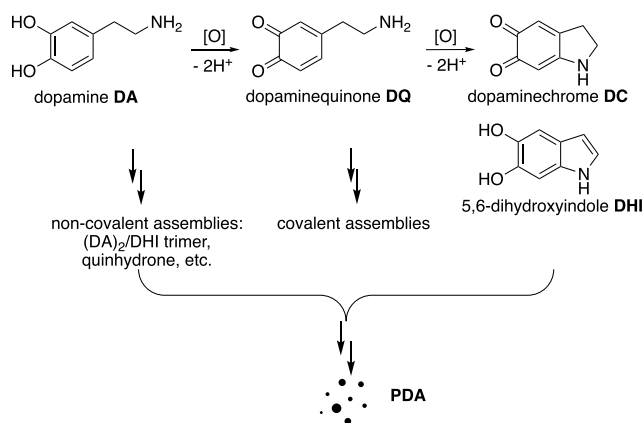
The most commonly used oxidant for dopamine adhesion is oxygen from the atmosphere under basic conditions.¹ A freshly prepared dopamine solution typically goes through fast color and opacity changes, from transparent and colorless, to pink, and then to brown before the formation of brown precipitate.¹⁵ Even though DA solution undergoes rapid dynamic changes,

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Scheme 1. Current Understanding of Dopamine Oxidation and Aggregation Mechanism



DA oxidation by oxygen is sluggish due to the low solubility of oxygen in aqueous solution¹⁰ and the low reduction potential.⁷ PDA film formation is slow and typically takes hours to days.¹ The films are heterogeneous and contain large aggregates on the surfaces.^{16,17} They are unstable toward acids, bases, and polar organic solvents due to the loss of unreacted DA and other noncovalently attached species.^{16,18–20} Postdeposition oxidation has been reported to improve PDA film stability.^{18,19} Other oxidants, such as pure oxygen,¹⁷ sodium periodate,²¹ copper sulfate,²¹ copper sulfate/hydrogen peroxide,^{16,22} and ammonium persulfate,^{21,23–25} have been evaluated. The use of stronger oxidants accelerates PDA film formation as well as improves the homogeneity and stability of the films.^{16,17,22,24}

The driving forces for surface adhesion of PDA include the aforementioned noncovalent and covalent interactions that hold PDA particles together and the coordination bonds formed between catechol moieties and some metal surfaces.² Ultimately, surface chemistry dictates the type of PDA-substrate interactions at play. It has been shown that surface hydrophobicity enhances the thickness of the adhered PDA films.^{26,27} In one study, PDA films were deposited on native and modified silicon wafers containing $-\text{OH}$, $-\text{NH}_3^+$, $-\text{Ph}$, and $-\text{CH}_3$ functional groups, using atmospheric oxygen as the oxidant. AFM images show granular morphologies of all the PDA films and that nucleation density and growth rate are proportional to surface hydrophobicity.²⁷ Another study reports substrate-dependent PDA degradation rate.²⁸ However, the precise relationship between PDA film characteristics (growth kinetics, morphology, and stability) and PDA-substrate interactions remains unknown.

Dip-coating is the most widely used PDA deposition method. It involves immersing an object of interest in a DA solution for a prescribed amount of time. It does not require special equipment and is applicable to a variety of sample shapes. The disadvantages are that it may consume a large amount of solution and that there may be complications involved with moving samples across air-solution interfaces. Recently, spray-coating has been reported for PDA coating applications.^{29–32} It entails spraying a DA solution onto an object of interest for a brief period of time. Spray-coating is fast and consumes a small amount of solution. However, it may be challenging to achieve uniform PDA coatings without access to specialized equipment. Among the existing work, only freshly prepared dopamine solutions have been utilized for PDA depositions except for one study where a silicon wafer was

immersed in a DA solution that had been aged for 24 h, with the intent of studying surface adhesion of large PDA aggregates.¹⁰ Spin-coating is another common coating method. It consists of four basic steps: deposition, spin up, spin off, and solvent evaporation.³³ It has similar advantages as spray-coating, and requires a spin-coater to achieve uniform thin films. To the best of our knowledge, its application in PDA deposition has not been reported. Recently, we reported a modified spin-coating method, adsorptive spin-coating, which is a hybrid of dip-coating and spin-coating.³⁴ A deliberate, optimized, yet short adsorption step prior to spin sets this approach apart from other thin film fabrication techniques.

In this study, we hypothesized that PDA adhesiveness goes through a maximum as dopamine oxidation and aggregation progress and that this maximum occurs in a very brief period during the reaction/adsorption process. Our main focus was to determine the optimal dopamine solution aging time for PDA surface adhesion while surveying other common reaction parameters. Oxygen and sodium periodate were chosen as representatives of a weak and a strong oxidant, respectively. In the sodium periodate trials, solution pH and dopamine concentration were varied to have access to different reaction rates. Three substrates were evaluated to study the effect of surface chemistry and hydrophobicity on PDA thin-film morphology and stability. In this study, we demonstrate that adsorptive spin-coating is an ideal fabrication method for PDA thin films because it permits the deposition of an aged DA solution, the capture of adhered PDA particles during an allotted adhesion period, and the rapid removal of excess solution.

EXPERIMENTAL SECTION

Materials. Silicon wafers (SiO_2 , 100 orientation, P/B doped, resistivity 1–10 $\Omega\text{-cm}$, thickness 475–575 μm) were purchased from International Wafer Service. Dopamine hydrochloride (DA, 99.8%), sodium carbonate monohydrate (ACS grade), and sodium bicarbonate (ACS grade) were obtained from Sigma-Aldrich. Sodium periodate (SP, 99%) was purchased from Acros Organics. Glacial acetic acid (ACS grade), dimethyl sulfoxide (DMSO, 99.9%), sodium acetate trihydrate ($\geq 99\%$), and 0.1 M hydrochloric acid (HCl, ACS grade) were obtained from Fisher Scientific. Trimethylsiloxy-terminated polydimethylsiloxane (PDMS, M.W. = 9 kDa) and 4–5% aminopropylmethylsiloxane-dimethylsiloxane copolymer (PADMS, M.W. = 7 to 9 kDa) were purchased from Gelest. HPLC-grade toluene and acetone were obtained from Pharmco. Oxygen gas (99.999%) was purchased from Middlesex Gases Technologies. All reagents were used as received without further purification. Water was purified using a Millipore Milli-Q Biocel System (Millipore Corp., resistivity $\geq 18.2 \text{ M}\Omega/\text{cm}$).

Instrumentation and Characterization. Silicon wafers were cleaned in a Harrick PDC-001 plasma cleaner. Spin-coating was carried out using a Laurell WS-400B-6NPP/LITE single wafer spin processor. Contact angles were measured using a Ramé-Hart telescopic goniometer with a Gilmont syringe and a 24-gauge flat-tipped needle. Dynamic advancing (θ_A) and receding (θ_R) angles were captured by a camera and digitally analyzed while Milli-Q water in the syringe was added to and withdrawn from the drop, respectively. The standard deviation of the reported contact angle values is less than or equal to 2° unless specified otherwise. Native silicon dioxide and polymer layer thicknesses were measured using a Gaertner Scientific LSE Stokes ellipsometer at a 70° incident angle (from the normal to the plane). The light source is a He-Ne laser ($\lambda = 632.8 \text{ nm}$). Thickness was calculated using the following refractive indices: air, $n_0 = 1$; silicon oxide and polymer layers, $n_1 = 1.46$; silicon substrate, $n_s = 3.85$ and $k_s = -0.02$ (absorption coefficient). Measurement error is within 1 Å as specified by the manufacturer. Each reported thickness

and contact angle value is an average of at least eight measurements obtained from at least two samples from two different batches and four readings from different locations on each sample. Nanoscopic surface topography was imaged using a Veeco Metrology Dimension 3100 atomic force microscope (AFM) with a silicon tip operating in tapping mode. Roughness and section analyses of surface features were determined using Nanoscope software. Dynamic light scattering (DLS) measurements were carried out using a Malvern Zetasizer Nano-S equipped with a 4 mW He–Ne laser ($\lambda = 632.8$ nm). Refractive indices of PDA ($n = 1.590$) and water ($n = 1.330$) and viscosity of water ($\eta = 0.8872$) at 25 °C were assigned. A Cary 100 UV–visible spectrophotometer from Agilent Technologies was used to record UV–visible spectra of dopamine solutions.

Preparation of SiO₂, PDMS, and PADMS Substrates. Silicon wafers were diced into 1.2 × 1.5 cm pieces, rinsed with distilled water, dried with compressed air, and kept in a clean oven at 110 °C for 30 min prior to being exposed to oxygen plasma at ~300 mTorr and 30 W for 15 min. Wafers were removed from the plasma chamber after allowing charge neutralization for 15 min. A 100 μ L portion of PDMS or PADMS polymer was dispensed on each clean wafer. Samples were heated at 100 °C for 24 h in capped scintillation vials. The wafers were then rinsed individually with toluene (3 \times), acetone (3 \times), and Milli-Q water (3 \times) and dried under a nitrogen stream to remove excess water and in a desiccator (CaSO₄) overnight.

Preparation of DA Solutions. DA solutions of 2 and 4 mg/mL in 0.05 M carbonate buffer at pH = 8.5 were prepared for trials utilizing atmospheric oxygen as an oxidant. DA solutions containing SP ([DA] = 1, 2, and 4 mg/mL and [SP]:[DA] = 2) in 0.25 M acetate buffer at pH values of 3.4, 4.9, or 5.9 were prepared for trials utilizing SP as an oxidant.

Spin-Coating. A DA solution was allowed to age for up to 30 min. The aged DA solution (100 μ L on SiO₂ and 500 μ L on PDMS and PADMS; [DA] = 1, 2, or 4 mg/mL for the SP trials and 4 mg/mL for the oxygen trials) was dispensed onto a substrate secured on the spin-coater stage. After a desired amount of adhesion time, the sample was spun at 6000 rpm for 1 min. The sample was rinsed with Milli-Q water (3 \times) and desiccated (CaSO₄) overnight.

Dip-Coating. For the conventional dip-coating method, substrates were submerged in a freshly prepared DA solution ([DA] = 2 and 1 mg/mL for the oxygen and SP trials, respectively) for a prescribed amount of time. For the modified dip-coating method, substrates were submerged in an aged DA solution ([DA] = 4 mg/mL and [SP]:[DA] = 2) for 1 min. The samples were slanted at approximately 60° relative to horizon with the polished side facing down. In the oxygen trials, the DA solution was open to air. After reaction, Milli-Q water was added to each reaction vial to remove the PDA film at the solution–air interface prior to sample retrieval. In the SP trials, the DA solution was closed to air. After reaction, the samples were directly removed from the solution without adding water. Each sample was rinsed with Milli-Q water (3 \times) and desiccated overnight.

Stability Studies. PDA-coated samples were soaked either in 0.1 M HCl (pH 1) for 2 h or in DMSO for 2 h followed by submersion in Milli-Q water for 1 h. All samples were subsequently rinsed with Milli-Q water (3 \times) and dried in a desiccator overnight.

RESULTS AND DISCUSSION

Optimization of Spin-coating Conditions. In our initial assessment of using the spin-coating method for PDA thin-film fabrication, a range of reaction parameters were surveyed—type of oxidant, DA concentration, buffer pH, surface reaction (adhesion) time, and DA reaction (aging) kinetics. In this report, we use “aging” time and “adhesion” time to distinguish the two types of “reaction” time to avoid confusion. For ease of preparation, silicon wafers were chosen as the substrate for this part of investigation. Spin conditions were fixed at 6000 rpm for 1 min to rapidly capture the surface-adhered PDA films. After spin-coating, samples were thoroughly rinsed in Milli-Q

water to remove salt crystals from the buffer solutions prior to characterization.

DA solutions containing SP were first evaluated using spin-coating. To suppress interference from oxidation by atmospheric oxygen, reactions were carried out in acidic acetate buffers of pH = 3.4, 4.9, and 5.9. DA concentrations up to 4 mg/mL were evaluated because solubility becomes an issue at higher DA and SP concentrations in 0.25 M acetate buffers. Since dopamine oxidation and aggregation are dynamic processes, we hypothesized that the surface adhesive properties of the species in solution are time-dependent. Thus, an important reaction parameter investigated was DA aging time. A DA solution was prepared and allowed to age for up to 30 min prior to being dispensed on a silicon wafer substrate. To probe the effect of adhesion time, the DA solution was allowed to be in contact with the substrate for 1, 2, or 5 min prior to spin. Figure S1 depicts PDA film thickness as a function of aging time, adhesion time, DA concentration, and buffer pH. From a buffer of pH = 3.4, PDA films of less than 2 nm were obtained. Much thicker PDA films were produced from buffers of pH = 4.9 and 5.9. In general, PDA thickness is greatly enhanced by an increase in buffer pH, which signifies the effect of pH on reaction thermodynamics.¹¹ Furthermore, PDA thickness increases as adhesion time increases from 1 min, to 2 min, to 5 min. Nonetheless, 1 min adhesion time was chosen to ensure that the solution concentration does not change appreciably during the adhesion period (due to solvent evaporation) and that the entire process remains expeditious. More importantly, minimizing adhesion time allows for the probing of adhesive properties of reactive species during a small window of aging time.

The effects of DA concentration and aging time were examined further while keeping the buffer pH at 5.9 and the adhesion time at 1 min in the SP trials. The results are shown in Figure 1. It is not surprising that the thickest PDA films were generated from the highest DA concentration of 4 mg/mL. What is intriguing is that maximum PDA thicknesses were obtained at 5 min aging time among all the DA concentrations examined. This implies that (P)DA adhesiveness reaches a

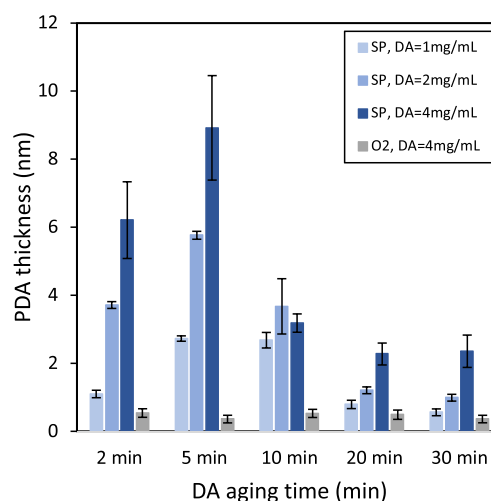


Figure 1. PDA film thickness on silicon wafer as a function of DA aging time and DA concentration in SP (pH = 5.9, blue) and oxygen (pH = 8.5, gray) trials using the spin-coating method while keeping adhesion time at 1 min, spin rate at 6000 rpm, and spin duration at 1 min.

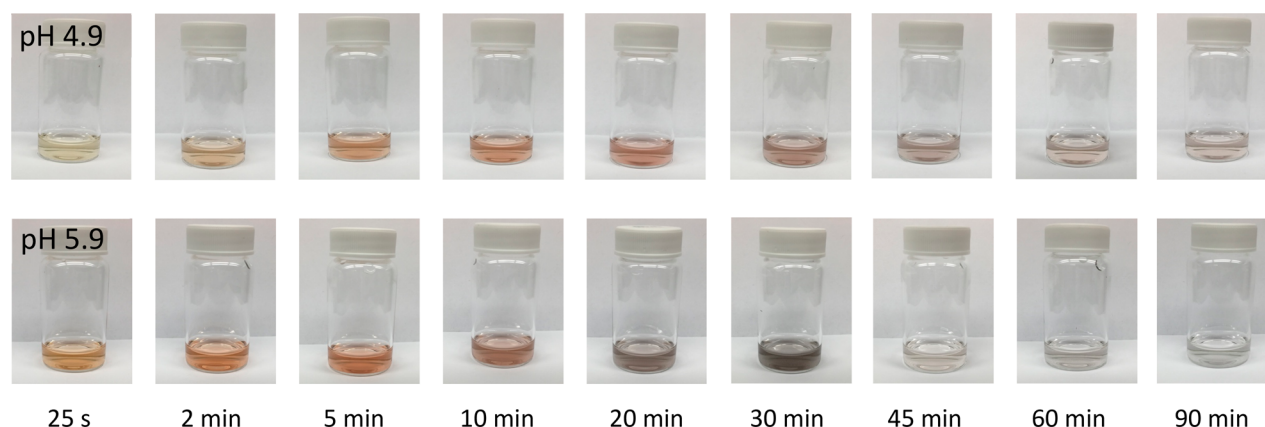


Figure 2. Photographs of DA (4 mg/mL) and SP in pH = 4.9 (top) and 5.9 (bottom) buffered solutions (diluted 100 \times) at aging times from 25 s to 90 min. Dilution was carried out using the top portion of the stock solutions immediately prior to characterization.

maximum as a function of DA aging time and that it is important to capture the time window in order to produce PDA films with appreciable thickness in a facile manner. Spin-coating provides the means to accomplish these objectives. In comparison, reactions involving atmospheric oxygen (pH = 8.5) using the highest DA concentration of 4 mg/mL did not result in much PDA adhesion (Figure 1). The much lower extent and rate of generating oxidative species using oxygen contribute to the lack of surface adhesion using the spin-coating method.

Dopamine Aging Kinetics in Solution. To provide insight into the surface adhesion trends demonstrated so far, dopamine aging kinetics in solution was investigated using color photography, UV-vis spectroscopy, and dynamic light scattering. We focus on comparing solutions containing the highest concentrations of dopamine (4 mg/mL) and sodium periodate ([SP]:[DA] = 2) in pH = 4.9 and 5.9 buffers, from which thick PDA films were produced (Figures 1 and S1).

The solutions at different aging times were diluted 100 \times prior to being photographed so that their color and opacity were more discernible. Photographs of the stock solutions are shown in Table S1 in the Supporting Information. As shown in Figure 2, both solutions changed from yellow, to orange, to gray, and to colorless as a function of aging time. The solutions also became noticeably opaque during the transition from orange to gray. As reaction progressed further, precipitates formed at the bottom of the stock solutions (Table S1 in the Supporting Information) and the diluted solutions taken from the top portion of the stock solutions appeared colorless (Figure 2). The main difference between the solutions at pH 4.9 and 5.9 is the faster color and opacity changes at the higher pH.

The evolution of the PDA particle size as a function of aging time at both pH values was probed by DLS, as shown in Figure 3. At pH 5.9, the PDA particles grew rapidly from the nanometer range (up to 5 min) to the micron range (starting from 10 min) and reached a maximum value of $\sim 1.6 \mu\text{m}$ (at 20 min) before decreasing back to the nanometer range (starting from 45 min). At pH 4.9, the trend was similar except that the maximum particle size was reached only after an aging time of 30 min. DLS results are consistent with the solution opacity shown in Figure 2. For example, the transition from orange to gray, or the onset of opacity, and the rapid increase of PDA particle size take place at aging time of 10 min at pH 5.9. Similar correspondences between PDA particle size and

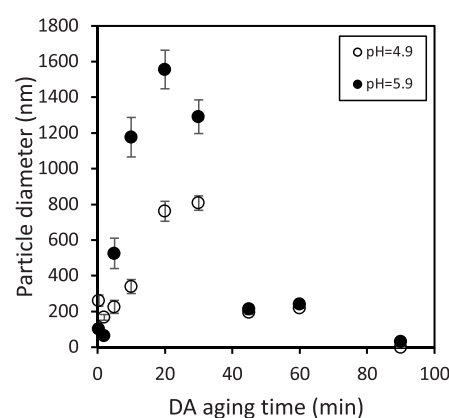


Figure 3. PDA-particle diameter in pH = 4.9 (open circles) and pH = 5.9 (filled circles) buffered solutions containing DA (4 mg/mL) and sodium periodate (diluted 100 \times) as a function of DA aging time. Dilution was carried out using the top portion of the stock solutions immediately prior to characterization.

solution opacity were also observed at pH 4.9. In addition, larger particle sizes were detected at pH 5.9, which is attributed to the thermodynamic favorability of product formation at higher pH.¹¹ Due to the heterogeneous nature of the solutions and that multiple dilutions were made, we do not attempt to quantify the disparity in particle size here. As a comparison, PDA particle size as a function of DA aging time in an oxygen trial is shown in Figure S2. The trend is similar; however, it took a few hours before the PDA particles reached a maximum size due to the slower reaction kinetics.

Time-resolved UV-vis spectra of the DA solutions oxidized by SP at pH 4.9 and 5.9 as well as by oxygen at pH 8.5 are shown in Figure 4. For the solution containing SP at pH = 4.9, a peak at 395 nm corresponding to the yellow dopaminequinone (DQ)^{35,36} appeared during the early stage of the reaction (Figure 4a). This peak was absent at pH 5.9 (Figure 4b), presumably due to the faster reaction kinetics and the larger extent of oxidation.¹¹ For both solutions, a peak around 480 nm corresponding to the orange dopaminedochrome (DC)^{36,37} was observed. The intensity of the peak increased first followed by a decline, caused by PDA particle precipitation at longer aging time (30 min at pH 4.9 and 2 min at pH 5.9). These observations are consistent with the color and opacity of the solutions shown in Figure 2. The region between 275 and 300 nm consists of absorption peaks of catechol at around 280

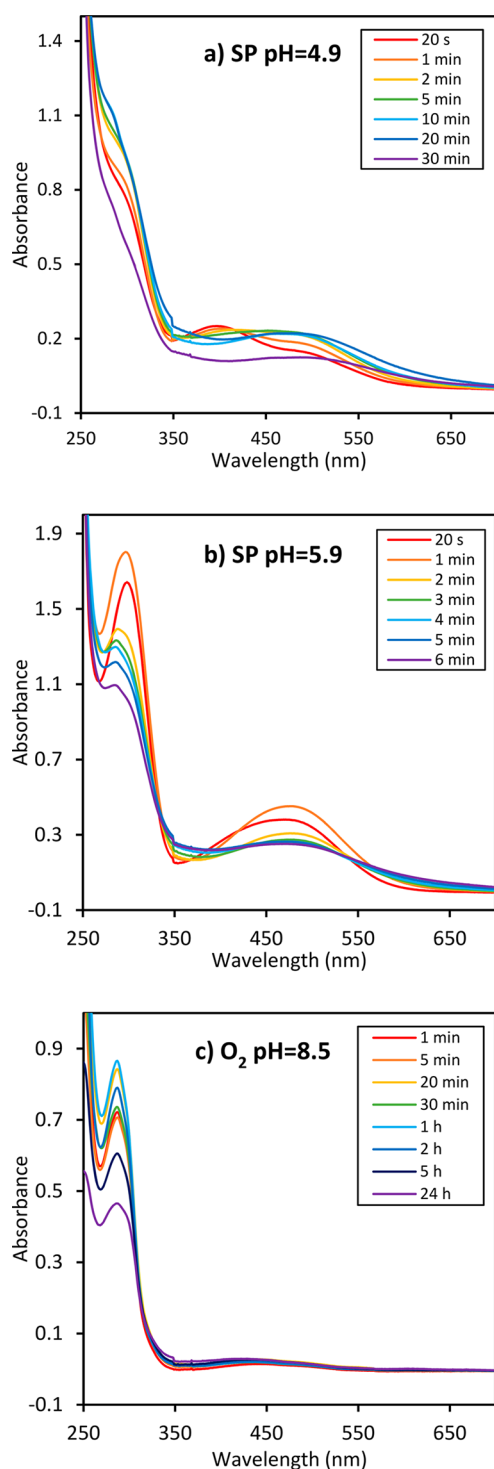


Figure 4. UV-vis spectra of DA solutions as a function of DA aging time. (a) DA (4 mg/mL) and sodium periodate in a pH = 4.9 buffered solution (diluted 100 \times). (b) DA (4 mg/mL) and sodium periodate in a pH = 5.9 buffered solution (diluted 100 \times). (c) DA (2 mg/mL) in a pH = 8.5 buffered solution (diluted 50 \times). Dilution was carried out using the top portion of the stock solutions immediately prior to characterization.

nm³⁸ and DC at around 300 nm.³⁷ Catechol and/or DC moieties appear to be more prevalent at pH 5.9 based on the stronger absorption peaks in this region. The spectra corresponding to the DA oxidation by oxygen (Figure 4c) do not show the characteristic DQ or DC peaks. Instead they

contain a low-intensity, broad peak at 420 nm corresponding to the formation of PDA.³⁹ The strong absorption peaks at around 280 nm indicate the abundance of catechol moieties, likely from unreacted dopamine. The formation of precipitates in all the DA solutions reduces concentrations of relevant species and introduces light scattering, prohibiting quantitative analysis using UV-vis spectroscopy.³⁶

The analyses of DA oxidation and polymerization in various solutions along with the spin-coating results on the silicon wafer substrate point to the stronger adhesive properties of DC. In the solution containing SP at pH 5.9, its presence was detected immediately (20 s in Figure 4b) giving rise to the formation of the thickest PDA film at the short aging time of 5 min (Figure 1). In the solution containing SP at pH 4.9, the DC peak did not appear until after 2 min so that the formation of the thickest PDA film was delayed to 10–20 min aging time (Figure S1). Furthermore, the PDA films formed in the pH 5.9 solution are thicker, indicating the stronger surface affinity of the DC-containing species. The pH affects both kinetic and thermodynamic aspects of PDA formation and adhesion based on the data shown thus far. The large PDA particles and their eventual precipitation (Figures 2 and 3) result in reduced surface adhesion at longer aging times (Figures 1 and S1). The slow oxidation kinetics and the absence of DC in the oxygen trials result in the formation of extremely thin PDA films using the spin-coating method (Figure 1).

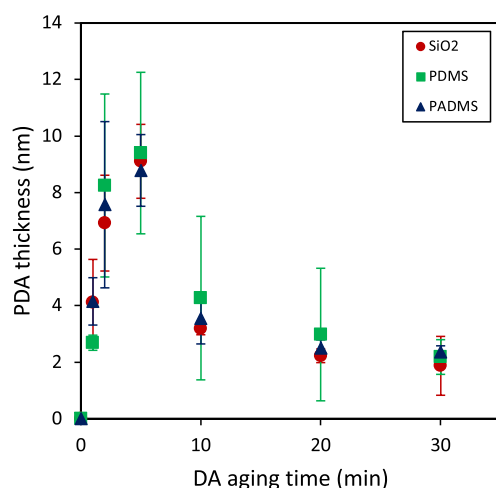
Effects of Substrate Chemistry. To investigate the feasibility of using the spin-coating method to fabricate PDA thin films on different types of substrates, PDMS and PADMS polymers were covalently attached to silicon wafers to impart different surface functionalities and wettability.⁴⁰ AFM images of the substrates (not shown) indicate that they are molecularly smooth with root-mean-square roughness values of ~ 0.3 nm. Table 1 provides relevant information on surface chemistry, nature of interaction with PDA, thickness, and contact angle values of the three substrates. Silicon wafer substrates contain a native oxide layer of SiO₂ and are hydrophilic. The surface silanol group, Si-OH, has a low pK_a value of ~ 4 .⁴¹ It can hydrogen bond with and electrostatically attract PDA. Both PDMS and PADMS substrates are hydrophobic and can have hydrophobic interactions with PDA due to the presence of the dimethylsiloxane group. Five percent of the repeat units on the PADMS polymer contain primary amine groups, which can have covalent bonding, hydrogen bonding, electrostatic attraction, and π -cation interaction with PDA.

Figure 5 depicts PDA thickness as a function of aging time on the three substrates using the spin-coating method. The optimized fabrication conditions obtained from the earlier section were employed. All three traces show the same trend: the PDA thickness increases initially and reaches a maximum value of ~ 10 nm at 5 min aging time before decreasing to ~ 2 nm at longer aging times. At 2 min aging time, the thickness values are considerably close to the peak values, especially after taking into account the high standard deviations on all the substrates at this time point. A two-factor ANOVA test indicates that aging time has a significant impact on PDA thickness (p -value $\ll 0.001$) while there is a negligible difference among the substrates (p -value = 0.19).

We note that the standard deviation values for the PDMS series in Figure 5 are significantly higher than the other two series (p -value = 0.04 based on an ANOVA test), which we attribute to the heterogeneous morphologies of the PDA films

Table 1. Three Substrates: Surface Functionality, Type of Interaction with PDA, Thickness, Advancing and Receding Contact Angles (θ_A/θ_R)

substrate	functionality	interaction with PDA	thickness (nm)	contact angles (deg)
SiO ₂	—OH/O [−]	hydrogen bonding, electrostatic	1.1 ± 0.1	8 ± 2/0 ± 2
PDMS	—CH ₃	hydrophobic	3.8 ± 0.1	107 ± 2/97 ± 2
PADMS	—NH ₃ ⁺ , —CH ₃	hydrophobic, hydrogen bonding, electrostatic, π -cation, covalent bonding	4.1 ± 0.1	103 ± 2/80 ± 4

**Figure 5.** PDA film thickness on SiO₂, PDMS, and PADMS substrates as a function of DA aging time using the spin-coating method while keeping pH at 5.9, DA concentration at 4 mg/mL, [SP]:[DA] at 2, adhesion time at 1 min, spin rate at 6000 rpm, and spin duration at 1 min.

on the PDMS substrate and the homogeneous coverage of the PDA films on the other two substrates as shown in Table 2.

Table 2. AFM Images of PDA Films on SiO₂, PDMS, and PADMS Substrates as a Function of DA Aging Time Using the Spin-Coating Method^a

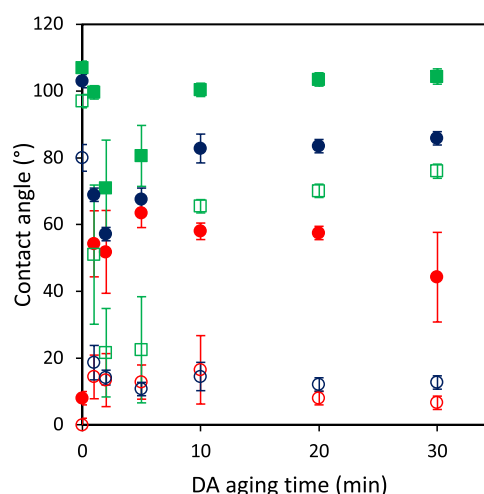
aging time	SiO ₂	PDMS	PADMS
1 min			
2 min			
5 min			
10 min			
30 min			

^aImage size: 1.25 × 5 μ m; height scale: 20 nm. Conditions: pH at 5.9, DA concentration at 4 mg/mL, [SP]:[DA] at 2, adhesion time at 1 min, spin rate at 6000 rpm, and spin duration at 1 min.

The AFM images indicate that the PDA film morphology and growth mechanism depend on the nature of the substrate-PDA interactions. On the silicon wafer and PADMS substrates, the adhered PDA particles appear as specks. Their density and size reach maxima at 2–5 min aging time, which is consistent with the thickness trend. The extent of PDA surface adhesion depends on the PDA particle size and chemistry. At short aging times, the particles are insufficiently oxidized and are too small to significantly contribute to surface coverage. At long aging times, the particles are too large to be adhesive. On the basis of the data scale of the AFM images, the size cutoff is \sim 20 nm. The PDA adhesion on the PDMS substrate undergoes a different mechanism. Irregularly shaped PDA “islands” form at

1 min aging time. They merge at 2 min aging time before decreasing in coverage at longer aging times. The island morphology indicates that the adhered PDA particles spread to maximize surface contact area, driven by hydrophobic interactions. It is important to note that cracks of different size and shape due to the incomplete merge of adjacent islands were observed on all the PDA films adhered to the PDMS substrate. PDA specks were also observed on PDMS obtained at 2 and 5 min aging time; however, they appear to be on top of an adsorbed PDA layer and are not in direct contact with the substrate. It is interesting that the PDA film morphology on the PADMS substrate is almost identical to that on the silicon wafer substrate even though the PADMS surface is close in hydrophobicity to the PDMS surface. The presence of a small percentage of amine groups apparently alters the interactions between the surface and the PDA particles (Table 1) so that the PDA particles do not spread on the PADMS substrate upon adhesion.

Advancing and receding water contact angles were measured on the spin-coated PDA films prepared at different aging times to discern surface wettability and coverage on various substrates, as shown in Figure 6. At 2–5 min aging time, the

**Figure 6.** Advancing (filled symbols) and receding (open symbols) contact angles of PDA films on SiO₂ (red), PDMS (green), and PADMS (blue) substrates as a function of DA aging time using the spin-coating method while keeping pH at 5.9, DA concentration at 4 mg/mL, [SP]:[DA] at 2, adhesion time at 1 min, spin rate at 6000 rpm, and spin duration at 1 min.

advancing contact angles exhibit minimum values on the hydrophobic PDMS and PADMS substrates and maximum values on the hydrophilic silicon wafer, indicating that maximum PDA surface coverages were achieved. In this window of aging time, similar advancing and receding angles (θ_A/θ_R) of \sim 60°/ \sim 15° were obtained on the silicon wafer and PADMS substrates. These dynamic contact angle values are consistent with those reported in the literature.⁴² The contact

angle values of the PDA films on PDMS are higher than those on PADMS due to incomplete surface coverage.

Comparison with Dip-coating Method. PDA films were also prepared using the conventional dip-coating method for comparison purposes. To slow down the reaction rate, DA concentration was reduced from 4 mg/mL to 1 mg/mL. Each substrate was immersed in a freshly made DA solution at pH 5.9 for up to 30 min. The AFM images of the PDA films (Table S2 in the Supporting Information) depict PDA specks on the silicon wafer and PADMS substrates as well as PDA islands and their growth on the PDMS substrate, suggesting that adhesion mechanisms are similar to the spin-coated PDA films on these substrates. The spin-coating method provides snapshots of surface adhered species during a brief time period as the DA solution ages while the dip-coating method permits continued accumulations of adhered species from the very beginning of the DA aging process. Therefore, continuous films were eventually achieved on the PDMS substrate at longer immersion time using the dip-coating method.

The most important knowledge acquired using the spin-coating method is that a critical duration of aging time is required for PDA particles to reach optimal adhesiveness. As a proof of concept, each substrate was immersed in an aged DA solution for 1 min to simulate the adhesion conditions used for spin-coating. The PDA films obtained as a function of aging time using the modified dip-coating method have almost identical characteristics in terms of thickness, wettability, and topography (data not shown here) as the ones prepared using the spin-coating method (Figures 5 and 6, Table 2). Our results indicate that the identification of the optimal aging time of a particular DA solution is the key to optimizing and expediting PDA coating processes independent of the coating method employed.

Stability of PDA Films. PDA film stability is paramount in its applications. Because silicon wafers are unstable in a base, PDA stability was only carried out in an acidic solution of pH = 1 and DMSO, a polar organic solvent in which PDA films were reported to exhibit the least stability.^{16,20} Stability comparisons were made between the two oxidants, between the two coating methods, and among the three substrates. All the samples tested had a similar initial PDA thickness of ~10 nm. The percentage of PDA thickness decrease under various conditions is shown in Figure 7. PDA films prepared in the oxygen trials exhibit considerable instability: 60% to 80% loss under the acidic condition and 25% to 40% loss in DMSO. In comparison, those prepared in the SP trials had less than 10% loss using the conventional dip-coating method and less than ~5% loss using the spin-coating method. The substantial stability difference between the two oxidants is attributed to the different extents of PDA oxidation as shown in Figure 4. The dip-coated PDA films are slightly less stable than those prepared by the spin-coating method in the SP trials. The AFM images of these films are shown in Tables S3 and S4 in the Supporting Information. There is no discernible morphological differences between the spin-coated PDA films before and after the stability test (Table S3). The density of the large PDA particles appears to be somewhat lower after the stability test on the dip-coated PDA films (Table S4). Due to the longer exposure time to the DA solution using the conventional dip-coating method (10 min) relative to the spin-coating method (1 min), there are likely more loosely attached PDA particles. Among the three substrates, PDA films are slightly less stable on PDMS, which we attribute to the incomplete surface

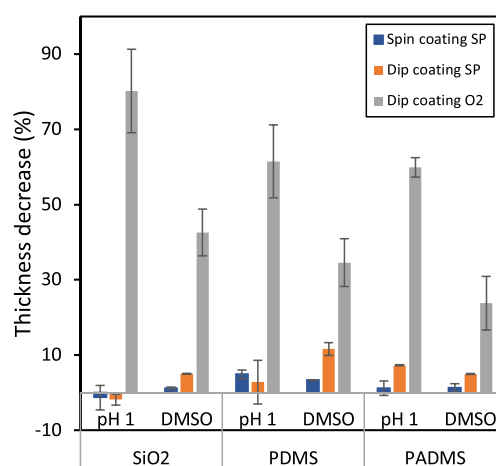


Figure 7. Percentage of PDA thickness decrease after soaking in aqueous solution of pH = 1 or DMSO for 2 h as a function of coating method, type of oxidant, and type of substrate.

coverage, hence the higher surface area. Overall, the spin-coated PDA films from the SP trials have excellent stability in acid and polar organic solvents.

CONCLUSION

A spin-coating method was assessed for PDA thin-film fabrication for the first time in this study. In order for the fabrication process to be expeditious and practical, it is necessary to choose a fast reaction system, such as the use of a strong oxidant and a high concentration of DA, and keep adhesion time short. More notably, DA aging time has been established to be an overlooked yet crucial parameter that affects PDA adhesiveness and PDA film thickness. The importance of DA aging time is the direct result of the dynamic nature of DA oxidation and aggregation and the evolving PDA particle size and chemistry over time. This concept was applied to a modified dip-coating method using the optimized reaction variants including the optimal DA aging time. Almost identical PDA films were produced as those obtained by using the spin-coating method.

The applicability of the spin-coating method for PDA thin-film fabrication was further evaluated on three different substrates with varying surface chemistry and hydrophobicity. PDA films of similar thickness and characteristics were obtained except that the growth mechanisms differed based on the type of substrate-PDA interactions. On the PDMS substrate where only hydrophobic interactions are present, the adhered PDA films consisted of irregularly shaped islands whose sizes varied as a function of DA aging time. On SiO₂ and PADMS where multiple types of interactions are at play, the PDA films consisted of specks and were continuous at the optimal DA aging time.

The stability of the PDA films in acid and DMSO was examined in terms of type of oxidant and fabrication method. The PDA films produced using sodium periodate as the oxidant and the spin-coating method have superior stability compared to those fabricated using the conventional dip-coating method and/or atmospheric oxygen as the oxidant.

In summary, PDA films of sufficient thickness and surface coverage can be fabricated on a wide range of substrates using the spin-coating method as long as a fast reaction system is utilized and an optimal DA aging time is identified. The

advantages are that the process is fast and the resulting PDA films are stable. This concept can be applied to other fabrication methods such as dip-coating and spray-coating.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.langmuir.9b02525.

PDA film thickness on silicon wafer as a function of various reaction parameters using the spin-coating method; photographs of DA solutions as a function of aging time; DLS of 2 mg/mL dopamine in pH 8.5 buffer as a function of DA aging time; AFM images of PDA films on SiO₂, PDMS, PADMS substrates as a function of immersion duration using the dip-coating method; AFM images of PDA films on SiO₂, PDMS, PADMS substrates before and after immersion in acid (pH = 1) and DMSO (PDF)

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Notes

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