UV-Triggered Dopamine Polymerization: Control of Polymerization, Surface Coating and Photo-Patterning

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Efficient surface modification strategies are crucial for the development of novel functional materials, surfaces and nanoparticles.[1] Among different surface coating methods, polydopamine (PD) coatings[2] have attracted great interest due to their ease and generality, as well as their applicability to almost any substrate.[2-4] A typical PD coating can be performed by immersing a substrate into a dopamine aqueous solution at basic pH.[2] In addition, PD coatings are reactive and can be post-modified by a variety of functional molecules, such as thiols,[2] amines,[5] acyl halides,[6] or by metal ions such as Ag^+ and Cu^{2+}.[2,7] Owing to these advantages, PD coatings were applied for new adhesive surfaces,[8a] for surface immobilization of proteins and nucleic acids,[8b,c] and for the formation of bio-arrays.[8d,e,f,g]

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These PD coated surfaces have been exploited to create anti-bacterial surfaces,[5a,8c] adhesive binders[8h], conductive electrodes[8i] as well as for the functionalization of nanoparticles.[7,8j,k,l] However, the current PD coating method exhibits some critical limitations. The main drawbacks are the inability to effectively control the onset and termination of the dopamine polymerization,[2,9] as well as the very slow kinetics of the process, which can take from several hours[10] to a few days.[2] This limits the scope of possible applications of dopamine polymerization and makes formation of functional PD micropatterns difficult.[2,8b,d,e,f,1,m]

Here, we report that dopamine polymerization can be triggered by UV irradiation. Moreover, the polymerization can be induced or stopped using UV light as a trigger. UV-assisted PD coating and photopatterning were demonstrated on different substrates. The UV-triggered dopamine polymerization and deposition was investigated by ellipsometry, X-ray photoelectron spectroscopy (XPS), X-Ray Reflectometry (XRR) and Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS).

A possible mechanism of dopamine polymerization is shown in Figure S1. Dopamine is first oxidized and rearranged/further oxidized into different quinone structures, which finally participate in the polymerization step. It has been shown that partial removal of oxygen by purging with argon slows down the kinetics of dopamine polymerization,[2] indicating an important role of oxygen in this process.[9] In addition, basic conditions (pH 8.5) are required to promote and accelerate the dopamine-quinone oxidation and the dopamine polymerization (Figure S1).[9b] However, strong oxidants, such as ammonium persulfate and sodium periodate, were shown to induce dopamine polymerization even under neutral or acidic conditions.[9c,12a]

Reactive oxygen species (ROS), including singlet oxygen ($^1O_2$), superoxide radicals ($O_2^{-\cdot}$), or hydroxyl radicals ($\cdot OH$), are more active than molecular oxygen and are known to be generated under UV irradiation.[12] Taking this into account, we hypothesized that ROS could play the role of the oxidant required to initiate the dopamine polymerization, thereby controlling the process *in situ* upon UV irradiation (**Figure 1**).

In order to verify that dopamine polymerization can be initiated by UV light, the UV-Vis spectra of dopamine solutions (2 mg/ml) were measured after UV irradiation. The experiment was performed using Tris buffer solutions at pH 8.5 (commonly used for PD coatings[2]) and at pH 7.0 (at which dopamine polymerization is usually very slow). The solutions were irradiated with UV light (260 nm, 7.5 mW cm^{-2}, HgXe lamp) to achieve continuous generation of ROS. **Figure 2** shows the time-dependent change of color (Figure 2a) as well as the change of absorbance at 420 nm (Figure 2b) of the irradiated dopamine solutions (open symbols), and the non-irradiated samples used as a control (filled symbols). As depicted on Figure 2a, for dopamine solutions at pH 7.0, UV-irradiated solutions turned dark yellow after 2 hours, while the color change was almost imperceptible in the non-irradiated solutions.

The observed color changes were also confirmed by the UV-Vis spectroscopy (Figure 2b and S3). The absorbance at 420 nm of the irradiated sample increased from 0 to 1.4 after 2 hours of irradiation, while the non-irradiated solution showed only a small absorbance change from 0 to 0.26 (Figure 2b). The basic solutions at pH 8.5 exhibited the same tendencies. UV-irradiated solutions showed darker color (Figure 2a) and higher change in the UV-Vis absorbance at 420 nm after 2 hours of UV (Figure 2b, 0 - 1.6 under UV, and 0 - 0.75 in the dark). Moreover, for the dopamine solutions at pH 8.5, precipitation of large PD particles visible with the naked eyes was observed after 90 min of UV irradiation. On the contrary, no PD particles were observed in the non-irradiated samples after 120 min. The above experiments clearly indicate that UV irradiation accelerates dopamine polymerization.

Previously, it was shown that polymerization of dopamine under acidic conditions was completely inhibited in the absence of strong oxidants,[9b,13] which was confirmed by our results (Figure S4). However, the irradiation of the dopamine solution with UV light triggered the dopamine polymerization even under acidic conditions (Figure S4). On the other hand, we also observed a clear decrease of the kinetics of dopamine polymerization upon decrease of pH from 8.5 to 2.0 (Figure S4).

According to the previous reports, dopamine polymerization under basic conditions can be slowed down by reducing the amount of O_2 in the solution, which plays the role of an oxidant in the course of dopamine polymerization. In order to test whether the dopamine polymerization under UV light is based on a possible radical mechanism, oxygen-rich and oxygen-scarce argon-purged solutions were irradiated with UV light as well as were kept in the dark. The results (Figure S5) showed that the reduction of oxygen in the dopamine solution led to a decrease in the polymerization kinetics even under UV irradiation. Since oxygen is well known for its ability to trap radicals and inhibit radical polymerization, the result confirmed that UV-initiated dopamine polymerization was not based on a free radical mechanism.

The observed acceleration of the dopamine polymerization under UV light may be explained by ROS, which can be generated even from traces of O_2. To confirm that UV-triggered dopamine polymerization is an oxidation-induced process, 2 mg/mL of ascorbic acid (vitamin C, an efficient antioxidant and ROS scavenger)[14] was added to the dopamine solution in order to avoid the generation of ROS during UV irradiation. No polymerization was observed even after 2 hour UV irradiation at pH 7.0 or at pH 8.5 (Figure S6a). This confirms that UV-triggered dopamine polymerization also depends on dopamine oxidation which can be triggered by ROS. Additionally, we also showed that hydroxyl radicals ($\cdot$OH, an active ROS), produced using the $Cu^{2+}+H_2O_2$ system,[15] could stimulate the dopamine polymerization at pH 7.0 without UV irradiation (Figure S6b).

The half-life of the generated ROS is usually very short (e.g., ~4 μs for singlet oxygen in water, 1 μs for hydroxyl radicals).[16] Taking this into account, we hypothesized that under neutral and acidic conditions, UV triggered dopamine polymerization can be controlled by the UV dose. To investigate this, an argon-purged dopamine aqueous solution at pH 7.0 (Tris buffer) was irradiated with UV for 10 min (ON), followed by 30 min without UV (OFF). The ON-OFF cycle was repeated three times and the absorbance of the solution at 420 nm was

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tested after each step. The result depicted in Figure 2c shows that absorbance of the dopamine solution only increases upon UV irradiation. No absorbance increment was observed when the solution was not irradiated. This phenomenon can be explained by the high reactivity and short half-life of the UV generated ROS. Thus, as opposed to the base-induced dopamine polymerization, the UV-triggered polymerization at neutral or acidic pH can be conveniently controlled by properly regulating the "ON/OFF" mode of the respective irradiation.

Having shown the effect of UV irradiation on triggering and controlling dopamine polymerization, UV-promoted formation of PD layers on silicon substrates was investigated by ellipsometry, X-ray Photoelectron Spectroscopy (XPS), X-Ray Reflectometry (XRR) and Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS).

Four silicon wafers coated with PD under the following conditions were explored: (a) dark, pH 8.5; (b) UV, pH 8.5; (c) dark, pH 7.0; (d) UV, pH 7.0. According to the XPS spectra (**Figure 3**a), the peak corresponding to nitrogen (N1s) was found only in samples prepared by UV-triggered dopamine polymerization (pH 8.5 and pH 7.0) and by non-irradiated base-catalyzed dopamine polymerization (pH 8.5), confirming the existence of PD on the substrates. C1s XPS data are presented in Figure 3b. For samples where PD coating was found ("UV, pH 8.5", "UV, pH 7.0" and "dark, pH 8.5"), N/C ratios were 1:6, 1:8 and 1:8, respectively. The last two N/C ratio values are the same as was previously reported for the PD structure.[2] However, the N/C ratio for the "UV, pH 8.5" sample (1:6) indicates possible binding of the Tris molecules to the PD.

A time-dependent ellipsometry measurement of the PD thickness on silicon wafers is shown in Figure 3c. An acceleration of PD deposition under UV irradiation is clearly observed. As shown in Figure 3c, for surfaces in neutral solution, without UV irradiation (dark, pH 7.0) no PD layer was formed on the wafer, while for the UV-irradiated samples (UV, pH 7.0), a PD layer of 4 nm was obtained after 2h of irradiation. Similarly, samples at pH 8.5 with UV irradiation exhibited higher PD deposition rate (~4 nm in 2h) than the non-

irradiated samples (~2 nm in 2h). These results confirm that UV irradiation can accelerate both the dopamine polymerization and formation of PD layers on solid surfaces.

With the purpose to validate the results obtained by ellipsometry, the thickness of PD coatings obtained after 30 min in the dopamine solution was also characterized by XPS. From the attenuation of the Si 2p substrate signal in XPS measurements and assuming a homogeneous overlay we estimated the PD thicknesses to be 1.3 nm, 0.4 nm and 0.8 nm for the "UV, pH 8.5", "dark, pH 8.5" and "UV, pH 7.0" samples, respectively. These values are close to those obtained by ellipsometry (1.8 nm, 0.5 nm and 0.5 nm, respectively). X-Ray Reflectivity (XRR) measurement was also employed to confirm the results of the ellipsometry (Figure S7). The morphology and thickness of a UV-triggered PD layer prepared on a silica surface was also measured by AFM and the result confirmed the formation of a homogeneous PD layer of several nm thickness with a nanostructured surface (Figure S8 and Figure S9).

The structure of UV-triggered PD was investigated by ToF-SIMS. Figure 3d shows the negative ion mass spectrum of the PD formed by UV-triggered polymerization (30 min UV irradiation, pH 7.0, Tris buffer). A strong signal corresponding to the dopamine dimer fragment can be observed at m/z 297. The results obtained by ToF-SIMS confirm that the UV-triggered PD has a similar structure to the base-triggered PD.

Considering that one of the major advantages of the base-induced PD coating is its applicability to different substrates,[2,8] we investigated the UV-triggered deposition of PD on glass, gold, silicon wafer and alumina surfaces (Figure S10). The water contact angles (WCA) on these surfaces varied from 11~64° before coating and changed to ~40° after 30 min of UV irradiation at pH 7.0, indicating coverage of the substrates with a PD layer.

One of the main advantages of all photochemical surface functionalization methods is the ability to create two-dimension functional surface patterns. Formation of 2D patterns of PD using the base-catalyzed method is difficult due to the poor controllability of the polymerization. Here we show that the UV triggered PD deposition is perfectly suited for the

formation of 2D PD surface patterns. As shown in Figure 3c, no PD is deposited on the silicon wafer after 120 min in neutral solution without UV light, while a 4 nm PD layer is obtained in the corresponding UV-irradiated sample. **Figure 4**a depicts the TOF-SIMS mapping results of a PD pattern prepared by irradiating a dopamine solution (2 mg/ml) at pH 7.0 through a photomask (see supporting information for details). Figure 4b shows a microscopy image of a silver nanoparticle pattern, which is formed by immersing a PD pattern, produced on a porous polymethacrylate substrate, into a 50 mM $AgNO_3$ aqueous solution for 18 hours.[2] Figure 4c shows a fluorescence image of a dye pattern formed by immersing the PD pattern in a Rhodamine-SH solution for 24 hours, followed by washing with acetone.

In conclusion, a novel method allowing for the effective control of dopamine polymerization by UV light has been reported. Irradiation of a dopamine solution with UV light at both acidic and basic conditions showed a strong increase in the absorption of the solution at 420 nm – a characteristic peak of PD. Interestingly, the decrease of oxygen concentration in solution slowed down both the UV- and base-stimulated dopamine polymerization, indicating that both reactions involve an oxidation step and require oxygen. Additional experiments showed that ROS, such as hydroxyl radicals could accelerate the dopamine polymerization even under acidic conditions, while the addition of a ROS scavenger, could inhibit both the base- and UV-induced polymerization of dopamine at different pH. This indicates that the UV-triggered dopamine polymerization is based on the ROS generated under UV irradiation. Owing to the short half-life of ROS, we showed that the UV-induced dopamine polymerization could be easily controlled by the UV light (ON/OFF possibility). The UV-induced dopamine polymerization could be used to coat different materials including glass, silicon, or gold. It was also shown that the method was compatible with photopatterning and could be used to generate micropatterns of PD coating on different materials. The photopatterning method can potentially be employed on curved surfaces,

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porous surfaces, or particles, where the micro contact printing method is difficult to apply. We anticipate that the presented evidence for the UV-induced dopamine polymerization as well as the ability to form precise surface micropatterns of PD will lead to various applications of this method in the development of novel functional surfaces, materials, and devices.

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

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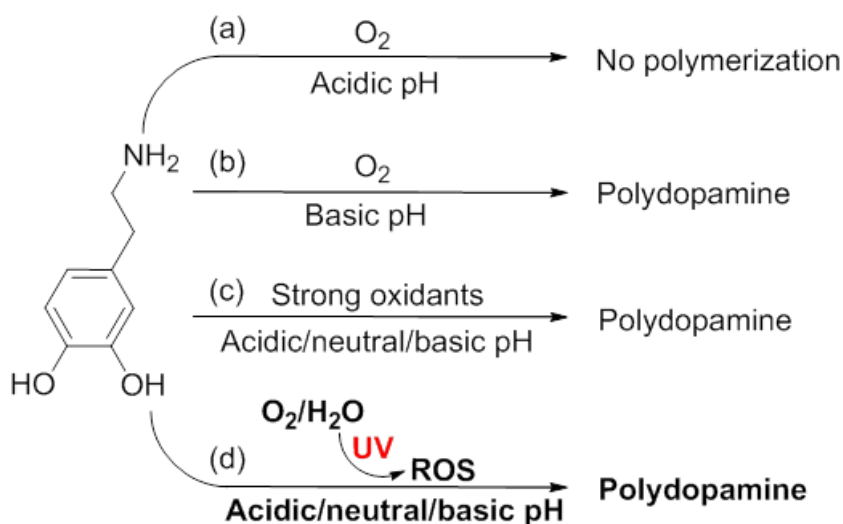
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Figure 1. Dopamine polymerization under different conditions. a) Acidic conditions – no polymerization.[9b] b) Basic conditions – fast polymerization.[2,9b] c) Acidic, neutral or basic conditions, with strong oxidants – fast polymerization.[9a,12a] d) Acidic, neutral or basic conditions, with UV irradiation – fast polymerization.
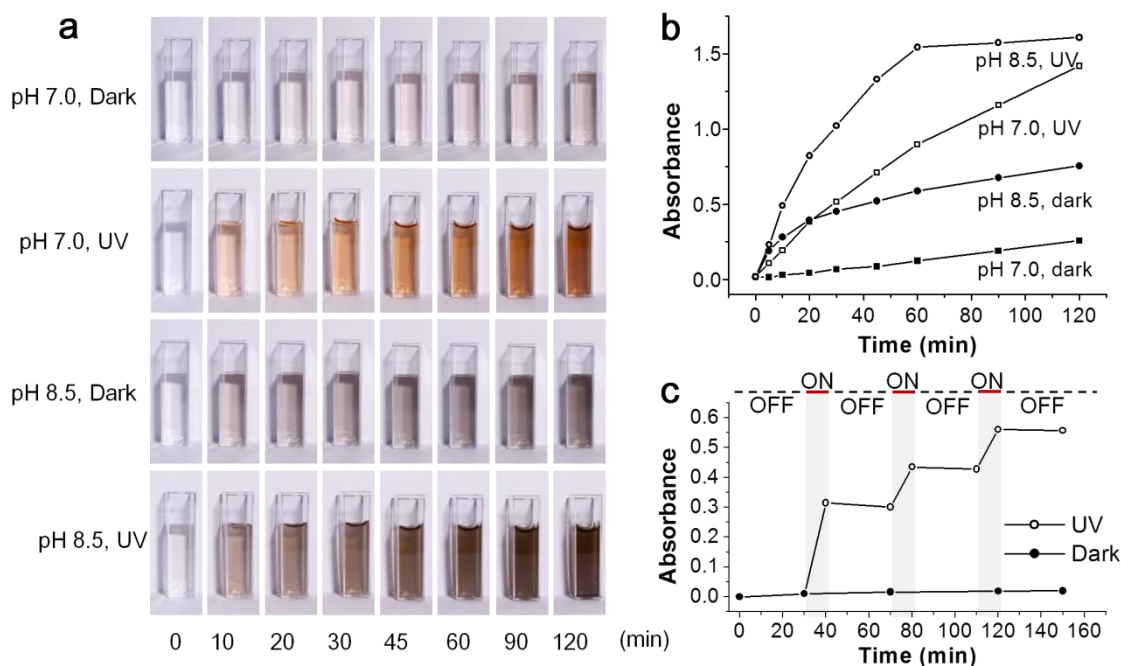

Figure 2 Color and absorbance change of dopamine solutions. a) Photographs of the corresponding dopamine solutions at different time points. b) Absorbance of the dopamine solution (2 mg/ml) at 420 nm as a function of time and pH. c) Change of absorbance (at 420 nm) of a low oxygen containing dopamine solution under UV irradiation at 254 nm (○) and in the dark (●). Dopamine solution (pH 7.0, purged with argon for 10 min) was irradiated for 10 min, followed by 30 min in the dark. The cycle was repeated 3 times.
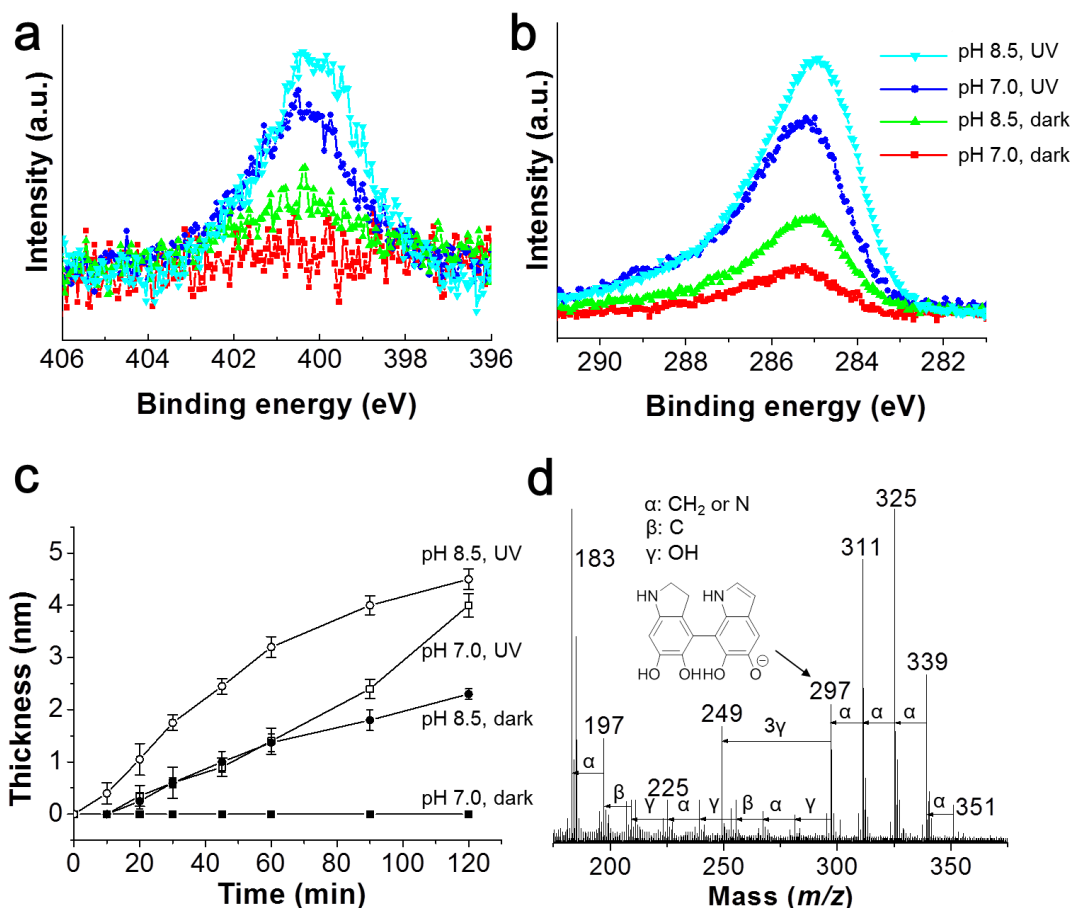
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Figure 3 Surface characterization on surfaces coated with UV triggered PD. a) N1s XP spectra of "UV, pH 8.5", "UV, pH 7.0", "dark, pH 8.5" and "dark, pH 7.0" samples. b) C1s XP spectra of "UV, pH 8.5", "UV, pH 7.0", "dark, pH 8.5" and "dark, pH 7.0" samples. c) Time-dependent PD thickness during the coating process, measured by ellipsometry. Samples: ○ pH 8.5, UV. ● pH 8.5, dark. □ pH 7.0, UV. ■ pH 7.0, dark. d) ToF-SIMS spectrum obtained from the UV triggered PD surface. The mass spectrum of the coated PD (dopamine concentration 2 mg/mL, pH 7.0, UV for 30 min) shows a dimer structure of 5,6-dihydroxyindole, possibly fragmented from a long-chain polymer of similar composition. A series of peaks, referring to different fragments of the polymer, could be observed in the spectrum.
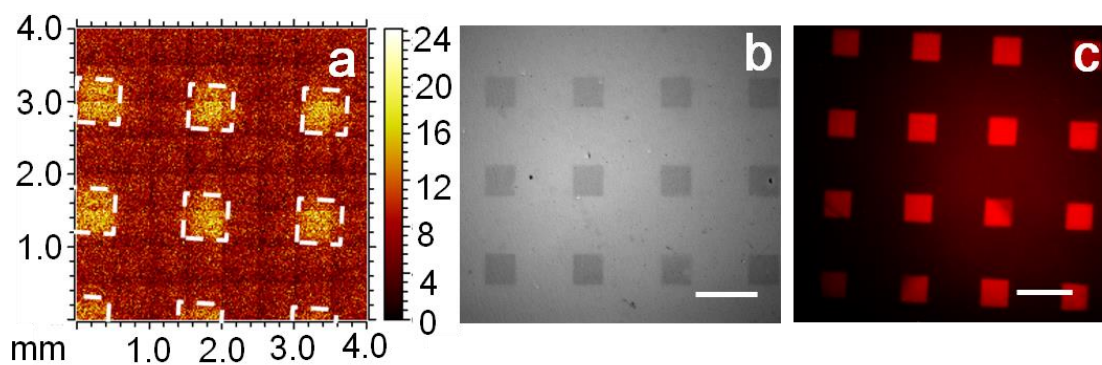
Figure 4 Photopatterning of PD. a) ToF-SIMS characterization of a PD pattern produced by photopatterning on a silicon wafer surface (CN$^-$ intensity map). b) Bright-field microscope image of a silver nanoparticle pattern produced on a PD patterned surface. c) Red fluorescence pattern formed by a treatment of the PD pattern with a Rhodamine-thiol solution . The scale bars are 1 mm.

Table of contents: We demonstrate that UV irradiation initiates dopamine polymerization and deposition on different surfaces under both acidic and basic pH. The observed acceleration of the dopamine polymerization is explained by the UV-triggered formation of reactive oxygen species that trigger dopamine polymerization. The UV-induced dopamine polymerization leads to a better control over polydopamine deposition and formation of functional polydopamine micropatterns.

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ToC figure