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$CuSO_4/H_2O_2$-Induced Rapid Deposition of Polydopamine Coatings with High Uniformity and Enhanced Stability

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Abstract: *Mussel-inspired polydopamine (PDA) deposition offers a promising route to fabricate multifunctional coatings for various materials. However, PDA deposition is generally a time-consuming process, and PDA coatings are unstable in acidic and alkaline media, as well as in polar organic solvents. We report a strategy to realize the rapid deposition of PDA by using* $CuSO_4/H_2O_2$ *as a trigger. Compared to the conventional processes, our strategy shows the fastest deposition rate reported to date, and the PDA coatings exhibit high uniformity and enhanced stability. Furthermore, the PDA-coated porous membranes have excellent hydrophilicity, anti-oxidant properties, and antibacterial performance. This work demonstrates a useful method for the environmentally friendly, cost-effective, and time-saving fabrication of PDA coatings.*

Surface modification is closely connected to the design and application of advanced materials.[1] It is a widely used and effective method for constructing functional materials, and a series of strategies have been proposed to elegantly tune or even completely change the properties of bulky materials. Typical strategies include surface initiated graft polymerization,[2] layer-by-layer assembly,[3] spin-coating,[4] and Langmuir–Blodgett deposition.[5] Recently, there has been increasing interest in the mussel-inspired chemistry of dopamine for surface modification, owing to its merits of material-independent adhesion and post-functionalization accessibility.[6] Dopamine is a main component of adhesive proteins in mussel, and is able to form polydopamine (PDA) coatings on various material surfaces by oxidative polymerization in an alkaline aqueous medium. PDA coatings contain many functional groups, such as catechol, amine, and imine, which endow those PDA-coated materials with versatile functionalities and properties.[7] These coatings can not only improve the surface hydrophilicity,[8] but also present excellent biocompatibility for materials.[9] More importantly, they are able to act as an intermediate layer facilely for the post-functionalization of material surfaces by subsequent reactions. For example, PDA coatings have been used as a chemical agent to reduce metal ions and as a principle medium to induce surface mineralization for fabricating organic–inorganic composite materials.[10] Antifouling surfaces have also been constructed by covalently grafting amine- or thiol-terminated methoxypoly(ethylene glycol) on those PDA-coated materials.[6] In addition to these functions, mussel-inspired chemistry has also been used to fabricate water-repellent coatings and hydrophobic surfaces.[11]

The performances of PDA-coated materials are highly dependent on dopamine polymerization, PDA deposition, and coating stability. However, several scientific and technical issues remain unaddressed. One issue is the low formation rate of PDA coatings, which generally requires a time range of ten hours up to a few days.[6] To overcome this drawback, several methods have been developed, such as UV irradiation, oxidant promotion, and electrochemical actuation.[12] The deposition rate of PDA can be improved to some extent by these methods. However, typical PDA coatings are uneven, and there are large PDA aggregates on the coated materials, which influence or even obstruct their applications in smooth surfaces.[13] Another crucial issue is that PDA coatings are unstable in some media, such as polar organic solvents and acidic or alkaline aqueous solutions.[14] In these cases, post-functionalization and applications are limited for PDA coatings and their coated materials. Therefore, it still remains a tremendous challenge to develop facile strategies for the rapid construction of PDA coatings with high uniformity and improved stability.

Herein, we report a strategy to greatly accelerate the polymerization of dopamine and the deposition rate of PDA coatings by using $CuSO_4/H_2O_2$ as a trigger. In our cases, Cu^{2+} and H_2O_2 produce reactive oxygen species (ROS), including $O_2^{\bullet-}$ and $HO_2^{\bullet}$, as well as $OH^{\bullet}$, in an alkaline medium.[15] These radicals play a key role in the polymerization of dopamine and improve the deposition rate of PDA coatings.[12a] A small amount of $CuSO_4/H_2O_2$ can enormously enhance the deposition rate of PDA coatings on various substrates. In addition, our PDA coatings exhibit high uniformity and enhanced stability in organic solvents with strong polarity. Furthermore, polypropylene microporous membranes (PPMMs) after 10-min deposition realize hydrophilic modification both on the membrane surfaces and in the membrane pores. The constructed PDA coatings contain copper ions and catechol groups that endow the membrane surfaces with good antioxidant properties and antibacterial performance. To our knowledge, this is the first report to realize rapid deposition of PDA coatings with high uniformity and improved stability.

Figure 1 shows the color change and UV/Vis absorbance at 420 nm with reaction time for various dopamine solutions. The solution with $CuSO_4/H_2O_2$ turned to black within 40 min, and no visible particles are formed. The UV/Vis spectra

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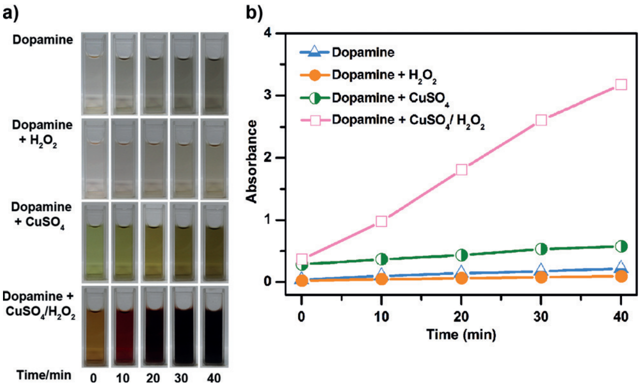

Figure 1. a) Photographs of original dopamine solutions with various additives ($CuSO_4$: 5 mM; H_2O_2: 19.6 mM) at different time points. b) Time-dependence of absorbance at 420 nm for various diluted dopamine solutions.

showed a characteristic peak at 420 nm, attributed to the polymerization of dopamine (Supporting Information, Figure S1).[12a] The absorbance gradually increased to 3.17, which is much higher than solutions of dopamine (0.22), dopamine with H_2O_2 (0.09) and dopamine with $CuSO_4$ (0.57; Figure 1 b). In this process, $CuSO_4$ acts as an oxidant to oxidize dopamine, and $CuSO_4/H_2O_2$ produce a large number of ROS to trigger dopamine polymerization. However, it should be noted that dopamine polymerization can be suppressed by H_2O_2. One possible reason is that H_2O_2 is an intermediate product of dopamine polymerization;[16] its high concentration could reverse the polymerization reaction to some extent. To confirm this, we studied the influences of H_2O_2 and $CuSO_4$ concentration on dopamine polymerization (Figure S2). The UV/Vis absorbance changed very slowly with increasing H_2O_2 concentration, while it increased at an astonishing speed after the addition of $CuSO_4$. Therefore, we could adjust the polymerization rate of dopamine by changing the ratio of $CuSO_4/H_2O_2$.

Dopamine polymerization is known to be key to the deposition rate of PDA coatings.[17] Figure 2 shows the results of PDA deposited on a silicon wafer using $CuSO_4/H_2O_2$ as a trigger. AFM images demonstrate the PDA coatings are composed of many nanoparticles. The average surface roughness (R_q) increases from 0.958 nm to 1.594 nm for those coatings deposited by 20 min and 40 min, respectively. By contrast, R_q increases from 1.27 nm to 8.88 nm when PDA coatings are deposited above room temperature (60 °C) and under vigorous stirring for 30 min.[18] Our $CuSO_4/H_2O_2$-triggered coatings show high uniformity, which is attributed to the rapid polymerization of dopamine and the homogenous nucleation followed by the quick deposition of PDA nanoparticles.[13a] As a result, the thickness of the PDA coatings increases linearly with the deposition time. Figure 2 d and Table 1 compare the thicknesses of various PDA coatings. Our $CuSO_4/H_2O_2$-triggered method showed the fastest deposition rate at room temperature, 43 nm h^{-1}, as high as 10 times than that of conventional methods. All of these results demonstrate that our method is a robust approach to rapidly construct PDA coatings with adequate thickness, uniform homogeneity, and conformal function, and therefore have great potential in the surface modification of various materials.

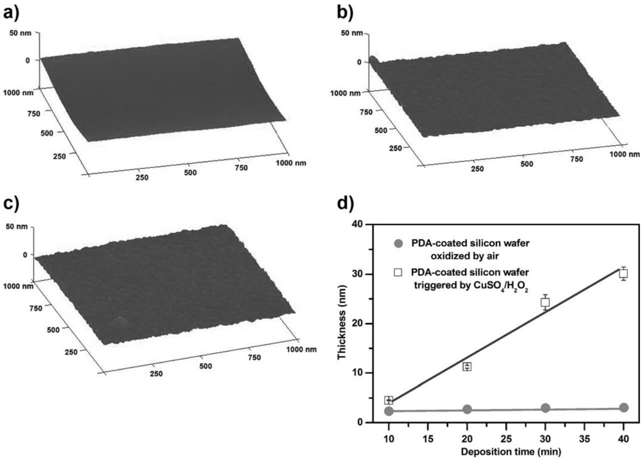

Figure 2. AFM images of the PDA-coated silicon wafer triggered by $CuSO_4$ (5 mM)/H_2O_2 (19.6 mM) for different times: a) 0 min, b) 20 min, and c) 40 min. d) Time-dependence of thickness for the PDA coatings deposited on silicon wafers, as determined by ellipsometry.

Table 1: Thicknesses of PDA coatings deposited with different methods.

Condition	Time [h]	Thickness [nm]	Thickness/Time [nm h^{-1}]	Ref.
Air, pH 8.5	24.0	50.0	2.1	[6]
Pure O_2, pH 8.5	0.5	4.4	8.8	[13a]
UV, pH 8.5	2.0	4.0	2.0	[12a]
$K_2S_2O_8$, pH 7.0	2.0	70.0	35.0	[12b]
$CuSO_4$, pH 8.5	80.0	70.0	0.9	[12c]
0.5 V, pH 6.0	1	11.5	11.5	[12d]
Air, pH 8.5	0.7	3.2	4.5	–[a]
$CuSO_4/H_2O_2$, pH 8.5	0.7	30.1	43	–[a]

[a] This work.

In addition to silicon wafers, our PDA coatings can also be rapidly deposited on other dense or porous substrates. The surface color of these substrates, including glass sheets, porous membranes, and polyester sponges, turned black or brown (Figure 3). Subsequently, the PDA-coated surfaces are able to efficiently induce the reduction of Ag^+ and the decoration of Ag nanoparticles on the substrates (Figure S3), and then to turn the surface color deeply dark. These PDA-coated and Ag-decorated substrates can be applied in various fields, depending on their dense to porous structures.

Chemical stability is a crucial feature for PDA coatings in practical applications. To investigate the coating stability, samples with the same PDA weight gains (Figure S4) were immersed in strong acid and alkali solutions, or polar organic solvents, for 2 hours. Elution amounts were measured, and a low value represents high stability for the PDA coatings. Figure 4 a showed that, when the PDA coatings were deposited by air oxidation, the elution amount increased dramatically with the polarity increase of the organic solvent, reaching 12.8 ± 2.36 %, 38.0 ± 4.37 %, and 73.5 ± 0.95 % in acetone, DMF, and DMSO, respectively. In contrast, the $CuSO_4/H_2O_2$-triggered coatings hardly eluted with these organic solvents. Furthermore, the coatings were relatively

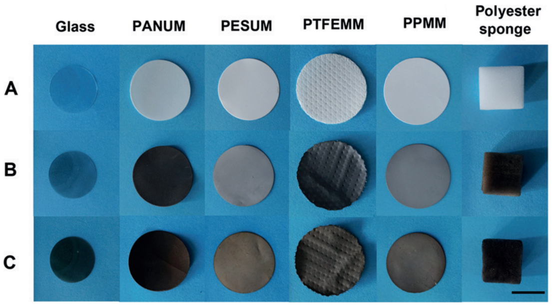

Figure 3. Digital photographs of A) nascent substrates, B) PDA-coated substrates after 40 min deposition, and C) PDA-coated substrates decorated by Ag nanoparticles. PANUM: polyacrylonitrile ultrafiltration membranes; PESUM: polyethersulfone ultrafiltration membranes; PTFEMM: polytetra-fluoroethylene microfiltration membranes; and PPMM: polypropylene microfiltration membranes.

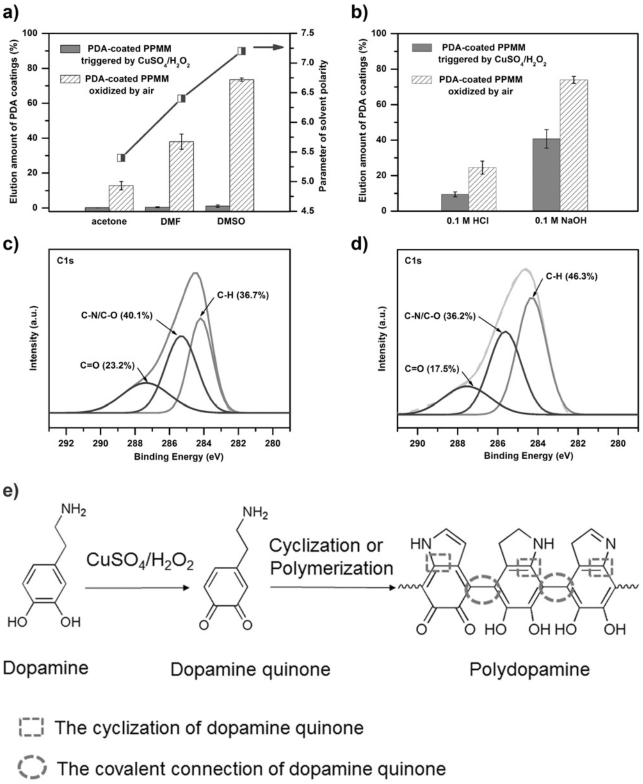

Figure 4. a) Elution amount of the PDA-coated PPMMs immersed in different organic solvents: DMSO, DMF, and acetone. b) Elution amount of the PDA-coated PPMMs immersed in different aqueous solutions: 0.1 M HCl and 0.1 M NaOH. c) High-resolution XPS spectra of PDA coatings on silicon wafer triggered by $CuSO_4$ (5 mM)/H_2O_2 (19.6 mM) for 40 min. d) High-resolution XPS spectra of PDA coatings on silicon wafer oxidized by air for 12 h. e) Illustration of the reduction of C−H during the process of dopamine polymerization.

stable in acid and alkali environments (Figure 4b). These results demonstrate the stability of PDA coatings are tremendously improved by using $CuSO_4/H_2O_2$ as a trigger (Figure S5 and Figure S6). Additionally, our $CuSO_4/H_2O_2$-triggered PDA coatings are more stable than those triggered by other oxidants, such as $(NH_4)_2S_2O_8$ and $NaIO_4$ (Figure S7). XPS was used to characterize the differences between these coatings. Figure 4c and d show that PDA coatings triggered by $CuSO_4/H_2O_2$ have a higher degree of oxidation than by air oxidation. Furthermore, the former coatings have a smaller ratio of C−H (36.7%) than the latter (46.3%). Figure 4e outlines a possible mechanism for PDA coatings triggered by $CuSO_4/H_2O_2$. The C−H ratio will be reduced both by the cyclization and covalent connection of dopamine quinone.[19] The two reactions result in many covalent parts and then stabilize the PDA coatings. It should be noted that the peaks at 954.27 eV and 932.27 eV are attributed to Cu $2p_{1/2}$ and Cu $2p_{3/2}$ (Figure S8). There are residual copper ions (2.41 mol%) in the coatings, which could act as cross-link sites by chelation with the amine and imine groups of PDA.[20] This could also improve the stability of PDA coatings dramatically.

PDA deposition has been regarded as an efficient and easy way to improve the surface hydrophilicity of various substrates, especially for porous membranes.[8] Our $CuSO_4/H_2O_2$-triggered process can turn PPMMs rapidly from white to black without morphology changes (Figure S9 and Figure S10). It is apparent that PDA coatings are uniformly deposited on the membrane surfaces (Figure S11). These coatings endow PPMMs with increased wettability. Figure 5a shows that the water contact angle (WCA) rapidly declined from 126° to 31.3° for the membrane deposited by 10 min only. The WCA finally decreased to less than 20° as the deposition time increased to 20 min. In addition, the water drop rapidly breaks into two parts and permeates through those membrane pores deposited by 40 min. (Figure S12). It is notable that a water drop has two behaviors on a porous membrane: spreading on the membrane surface and permeating into the membrane pores (Figure 5b). The permeation performance (I_P) can be evaluated by the wetting area ratio of the reverse membrane surface (S_R) and the top membrane surface (S_T). A higher I_P (S_R/S_T) indicates that the membrane

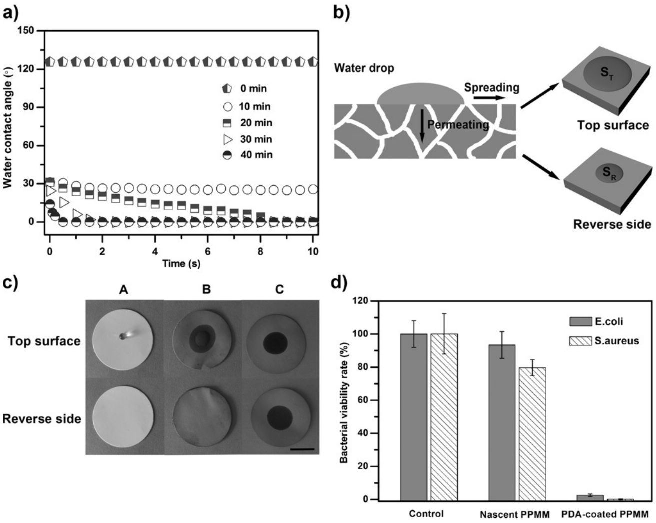

Figure 5. a) Water contact angle of the PDA-coated PPMMs triggered by $CuSO_4$ (5 mM)/H_2O_2 (19.6 mM) for different times. b) Illustration for the behaviors of a water drop on the hydrophilic surface of porous membrane. c) Digital photographs of a water drop (10 μL) on the membrane surfaces of nascent (A), PDA-coated with air oxidation (B), and PDA-coated with $CuSO_4/H_2O_2$ (C) triggering PPMMs (above) and the reverse sides of the membranes (below). d) Antibacterial activity of the nascent PPMM and the PDA-coated PPMM by 40 min rapid deposition with $CuSO_4/H_2O_2$ triggering. Scale bar = 1 cm.

possesses better permeation performance. Figure 5c shows that I_P is equal to 1 for the PDA-coated membranes triggered by $CuSO_4/H_2O_2$, while the value is 0 for those deposited by air oxidation. Similarly, the I_P value is also 0 for those deposited by other oxidants, such as $(NH_4)_2S_2O_8$ and $NaIO_4$ (Figure S13). These results indicate that the latter membranes exhibit hydrophilicity and wettability only on the membrane surfaces, whereas the $CuSO_4/H_2O_2$-triggered PDA-coated ones possess these properties both on the membrane surfaces as well as in the membrane pores. This was verified by XPS and EDX spectra from the membrane cross-section of the PDA-coated and Ag-decorated PPMMs (Figures S14 and S15).

We further evaluated the antioxidant property of the PDA-coated membranes by the 2,2-diphenyl-1-picrylhydrazyl (DPPH) assay, as PDA is a major pigment of eumelanin and can act as a radical trap in biological systems.[21] The high scavenging activity of DPPH indicated that the PDA-coated membranes have strong antioxidant property. When the assay time was 30 min, the DPPH solution turned from deep purple to light yellow and the scavenging activity reached 92% (Figure S16). The PDA coatings exhibited excellent antioxidant property and were able to efficiently protect the membrane surfaces. In addition, copper species show excellent antibacterial activity to a variety of bacterial strains as well as Ag.[22] As mentioned above, some copper ions are still chelated with the PDA coatings, which endow the membranes with good antibacterial performance toward *E. coil* and *S. aureus* (Figure 5d). It can be seen that about 97.4% of *E. coil* and 99.9% of *S. aureus* were killed during the antibacterial assay.

In conclusion, we have developed a useful method for the fast polymerization of dopamine and the rapid deposition of PDA coatings on various dense and porous substrates. The $CuSO_4/H_2O_2$-triggered PDA coatings possess adequate thickness, high uniformity, and enhanced stability. In addition, this rapid deposition is effective for the surface modification of porous membranes, which show excellent hydrophilicity, high water permeability, good antioxidant ability, and outstanding antibacterial performance.

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Keywords: antibacterial surface · dopamine · hydrophilicity · mussel-inspired chemistry · polydopamine coatings

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