Ultrasound expands the versatility of polydopamine coatings

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A B S T R A C T

Polydopamine (PDA) coating of surfaces is a versatile strategy to fabricate functional films on various substrates, which typically requires oxygen and alkaline pH. Overcoming such limitations may enhance the versatility of this technique. Herein, we develop a simple and green sonochemical process for PDA coatings, which overcomes the limitations of traditional coating technique and expands the versatility of PDA chemistry. The oxidizing radicals generated by high frequency ultrasound (412 kHz) are utilized to initiate and accelerate the polymerization of dopamine. The sonochemical rate of film deposition is found to be about twice faster than that of the traditional method in the presence of oxygen. Importantly, the PDA coatings can be obtained in neutral or acidic aqueous solutions and even in the absence of oxygen. The PDA coatings can be moderated by turning on or off high frequency ultrasound. This study provides an environmentally friendly and economic method for the engineering of PDA coatings independent of the solution pH and nature of dissolved gas.

1. Introduction

Mussel-inspired surface chemistry is a versatile method for surface functionalization, which has been used for drug delivery [1,2], anti-corrosion coatings [3,4], and wastewater remediation [5,6]. Dopamine is one of the most widely used polyphenols for surface coatings and has been proved to play an important role in adhesion processes [7]. The advantages of polydopamine (PDA) coatings lie in the versatility of the substrates that can be chosen, ease and scalability of the coating process, and flexible post-functionalization on PDA films based on Schiff base reaction or Michael addition, which provides a promising method for various applications such as tissue engineering and drug delivery [8–10]. The spontaneous autoxidation of dopamine to generate PDA films is a slow process and weak alkaline conditions and the presence of oxygen are typically essential. The need for alkaline pH and oxygen also limits the choice of substrates for coatings. The formation of PDA coatings usually takes many hours. Accelerating the formation of PDA coatings without being restricted by alkaline conditions and the presence of oxygen is challenging.

Recently, the addition of oxidants or biocatalysts has been proved to be an efficient way to accelerate dopamine polymerization for surface coatings. For example, the addition of CuSO 4/H 2 O 2 can shorten the coating time from hours to tens of minutes [11]. In this process, CuSO 4 and H 2 O 2 can generate a large amount of reactive oxygen species (ROS) to trigger the polymerization of dopamine in acidic conditions. Other oxidants, including sodium periodate [12], ammonium persulfate [13], laccase [14], and horseradish peroxidase [15], have been reported to significantly accelerate the PDA coatings. However, once the polymerization is initiated by the oxidants, it is difficult to terminate the reaction. Alternative approaches have been used to overcome this limitation of the use of oxidants, where ultraviolet (UV) and microwave irradiations are applied to accelerate the polymerization of dopamine [16,17]. In these polymerization processes, either ROS or local heating in the presence of oxygen increase the polymerization rates for surface coatings.

High frequency ultrasound with an ultrasonic frequency greater than 100 kHz can generate a large amount of ROS. Water molecules can be split into hydroxyl and hydrogen radicals by acoustic cavitation [18]. The free radicals generated by the ultrasonic process have shown promising applications in food processing [19], water remediation [20,21], nanoparticle formation [22,23], and polymer synthesis [24,25]. In our previous studies, sonochemistry have been used to
synthesize polymers and nanoparticles for drug delivery [26,27].
Herein, we demonstrate that sonochemistry can initiate and signifi-
cantly accelerate dopamine polymerization for PDA coatings on various
substrates, including glass, polystyrene, stainless steel, silicon, and silica
substrates, even in acidic and/or anoxic conditions (Scheme 1). In the
process of high frequency ultrasound (412 kHz), homolysis of water
molecules within cavitation bubbles occurs, which leads to the forma-
tion of hydroxyl and hydrogen radicals. These radicals are involved in
the formation of PDA. Compared with the traditional method, sono-
chemistry shortens at least 50% of coating times to obtain the same
thickness of PDA films. In addition, the sono-induced polymerization
process can be controlled by turning on or off the ultrasound. Impor-
tantly, in the presence of high frequency ultrasound, polymerization of
dopamine can be achieved in acidic (pH = 5.5) and anoxic solutions. The
reported method provides a new avenue for PDA coatings on various
substrates, which can avoid the essential conditions of alkaline pH and
oxygen for the conventional PDA coatings.

2. Materials and methods

2.1. Materials

Dopamine hydrochloride was purchased from J&K Scientific Ltd.
(China). Tris(hydroxymethyl) aminomethane (Tris) was obtained from
Beijing Hwrk Chemical Ltd. (China). Sodium dihydrogen phosphate
anhydrous, disodium hydrogen phosphate dodecahydrate were pur-
chased from Sinopharm Chemical Reagent Co., Ltd. (China). Silicon
wafer and silicon dioxide wafer were bought from Tebo Technology Co.,
Ltd. (China). All solutions were prepared with Milli-Q water (18.2 MΩ cm).

2.2. Experimental details

2.2.1. Polymerization of dopamine

Dopamine solutions (2 mg/mL) with various pH were prepared in
Tris buffer (10 mM, pH 8.5 and 7.0) or phosphate buffer (10 mM, pH
5.5). Subsequently, dopamine solutions were sonicated or stirred
(without sonication) at 40°C for 4 h. When polymerization was per-
formed in the absence of oxygen, solutions were degassed by nitrogen
before polymerization for at least 30 min and maintained in nitrogen
atmosphere during the experiment. All experimental procedures
involving high frequency ultrasound were performed by a class A
generator & amplifier (AG1021, T&C Power Conversion, Inc.). A 412
kHz plate transducer (Model 6G12, Honda Electronics Co. Ltd.) was used
to deliver ultrasound into the reaction solution, where 412 kHz ultra-
sound could generate maximum radicals as previously reported [27].
The temperature was controlled by a water circulating system.

2.2.2. Preparation of PDA coatings

Glass slides were treated with piranha solution (a mixture of
concentrated sulfuric acid and 30% hydrogen peroxide with a volume
ratio of 7:3) for 15 min, followed by rinsing with water and drying with
nitrogen. Glass slides were incubated with dopamine solution (2 mg/
ml) in the presence or absence of ultrasound. PDA coatings on other
substrates were performed using a similar procedure, except for the
cleaning step where the substrates were cleaned in water and subse-
quently in ethanol using an ultrasonic cleaning bath (40 kHz, 100 W).

2.3. Characterisation

The morphology of the PDA coating was observed by scanning
electron microscopy (SEM, G300, Carl Zeiss). The absorption spectra of
dopamine solutions were measured by a UV–Vis spectrometer (UV-
2600, SHIMADZU) using a 1 cm path length quartz cuvette. X-ray
photoelectron spectroscopy (XPS, ESCALAB 250, Thermo Scientific) was
performed to analyze the elements and chemical bond of PDA coatings.
The wettability of different substrates with or without PDA coatings
was characterized by a contact angle measuring instrument (DSA100, Kruss).
The thickness of different PDA coatings was characterized by atomic
force microscopy (AFM, Bioscope Resolve, Bruker).

3. Results and discussions

To demonstrate that sonochemical polymerization of dopamine
could be achieved in the absence of oxygen, a series of polymerization
experiments were carried out in alkaline medium (pH 8.5) in the pres-
ence and absence of air (oxygen). As shown in Fig. 1a, dopamine poly-
merization occurred in the presence of oxygen, as indicated by an
increase in the absorption at 420 nm with an increase in reaction time.
The color of dopamine solution got darker due to the polymerization of
donmoe to PDA. Dopamine tends to be polymerized in an alka-
line solution containing oxygen and the mechanism of polymerization is
well-known (Fig. 1b) [28]. In contrary, the polymerization of dopamine
did not occur in atmosphere in an alkaline solution (Fig. 1c),
which indicated the importance of the oxygen for the conversion of
dopamine into PDA. For the conventional PDA polymerization, both
oxidation and cyclization of dopamine required the participation of
dissolved oxygen [29,30]. When the same solution was sonicated by
high frequency ultrasound, the absorption of dopamine solution
increased with an increase in sonication time and the color of the
dopamine solution became darker (Fig. 1d). This observation suggests
that PDA can be formed in the absence of oxygen using high frequency
ultrasound (Fig. 1e). The results presented in Fig. 1 confirm that dis-
solved oxygen in water is an indispensable catalyst for the conversion
of dopamine to PDA by conventional techniques [17], whereas such limi-
tations could be overcome by a simple sonication procedure.

The second limitation for using conventional polymerization of
dopamine is the need for an alkaline solution. In order to investigate
whether the sonochemical polymerization of dopamine could be used to
overcome this limitation, experiments were carried out in acidic solu-
tions (pH 5.5). From Fig. 2a and b, polymerization of dopamine did not
occur in acidic solutions in the presence and absence of oxygen. On the
other hand, sonochemical polymerization of dopamine occurred in
acidic solutions under oxygen and nitrogen atmospheres (Fig. 2c and d).

Further experiments were conducted in neutral pH conditions as well
and the results are summarized in Fig. 3, where similar conclusion was
obtained as from Fig. 2. Fig. S1a shows that polymerization proceeds
with time in alkaline pH in the presence of oxygen without ultrasound
and no polymerization occurs in the absence of oxygen. The data in
Fig. S1a also demonstrates that polymerization of dopamine occurs in
the absence of oxygen when sonication is applied, almost at a similar
level to that of conventional polymerization in the presence of oxygen.
The results are similar to those shown in Fig. 1. However, what is
interesting is the enhanced rate of polymerization observed when

Scheme 1. Sonochemistry-induced polymerization of dopamine and PDA
coatings in acidic and anoxic conditions.
ultrasound is applied during the conventional polymerization process (alkaline solution containing oxygen). Conventional polymerization was difficult to occur at neutral or acidic pH since no UV–Vis absorption was observed within 4 h under stirring regardless of the presence of oxygen (Fig. S1b and c). These results indicated the important role of solution pH and oxygen on the rate of conventional polymerization of dopamine. As reported previously, ROS can trigger the oxidative polymerization of dopamine in acidic conditions [31]. UV/Vis absorption peaks at around 480 nm indicated the formation of dopaminochrome (the cyclization product of dopamine quinone) [32]. The results in Fig. S1b and c indicate the formation of PDA in anoxic and acidic/neutral conditions with ultrasonic treatment. In the sonopolymerization process, the polymerization rate in alkaline conditions is two times higher than that in neutral conditions and three times higher than that in acidic conditions. A previous study has shown that the polymerization rate by autoxidation process decreases with a decrease in solution pH [33]. A general thermodynamic model has been reported that the oxidation and cyclization of dopamine is favoured at alkaline pH [33].

It is well known that sonication of an aqueous solution at high ultrasound frequencies can generate a large number of living free radicals through acoustic cavitation process [27]. Among the free radicals generated by ultrasound, hydroxyl radical is a powerful, efficient, non-selective oxidant, which could be used for the degradation of organic molecules and in polymer synthesis [20,26]. It can be anticipated that the strong oxidizing radicals generated during acoustic cavitation process can initiate oxidative polymerization of dopamine, as schematically shown in Fig. S2.

It should also be noted that sonopolymerization of dopamine may
not only be initiated by the oxidizing radicals generated, but also by the extreme conditions generated during cavitation process. Recently, it has been suggested that such oxidative polymerization reactions occur at the cavitation bubble/solution interface [34]. They have shown that the abstraction of a hydrogen atom on the benzene ring to generate a phenyl radical and the subsequent polymerization process are high energy processes that are facilitated by the extreme thermal conditions generated at the cavitation bubble surface.

Another observation to be discussed is the difference in the rate of sonopolymerization between oxygen and nitrogen saturated solutions. In Fig. S1, the sonopolymerization rate in the presence of oxygen is about twice of that in the presence of nitrogen regardless of the pH. This could be due to the generation of a higher amount of oxidative radicals in the presence of oxygen. It is known that the homolysis of water within cavitation bubbles leads to the formation of hydroxyl and hydrogen radicals. Hydrogen radical is a reducing agent that could be converted into oxidizing hydroperoxyl radicals by the reaction between hydrogen radicals and oxygen. Thus, a higher amount of oxidizing radicals are generated in the presence of oxygen. In N₂ atmosphere, hydrogen radicals are not converted into oxidizing radicals and hence only hydroxyl radicals contribute to the sonopolymerization of dopamine.

It is clear from the mechanism that the oxidizing radicals generated during sonication play a dominant role in initiating and accelerating the formation of PDA. One of the challenges of using conventional polymerization of dopamine for surface coating is controlling the extent of polymerization and hence the rate and thickness of the surface coating. The generation of oxidizing radicals by sonication can be manipulated simply by turning the ultrasound on and off. To demonstrate this

Fig. 2. Dopamine polymerization in acidic conditions. UV/Vis absorption spectra and color changes of dopamine solutions in the (a, b) absence and (c, d) presence of ultrasound. (b, d) Dopamine solutions were degassed and protected with nitrogen. (e) Scheme of dopamine polymerization in acidic conditions. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
capability, dopamine solutions (2 mg/mL, 10 mM Tris-HCl, pH 8.5, purged with air) were sonicated for 30 min (ON) followed by 30 min standby without ultrasound treatment (OFF). The absorbance increased when the ultrasound was on and did not change significantly when the ultrasound was turned off (Fig. 4), which indicated that the polymerization of dopamine and hence the rate and thickness of the surface coating can be controlled.

Since the high frequency ultrasound can accelerate dopamine polymerization even in anoxic and acidic conditions, it provides an approach for rapid formation of PDA coatings. To prove the versatility of sono-induced PDA coatings, glass, polystyrene, stainless steel, silicon, and silica substrates were examined for PDA coatings at pH 8.5 in the presence of air. The color of the substrates after PDA coatings in the presence of ultrasound was darker than that without ultrasound treatment at the same time points (Fig. 5a). The formation of PDA coatings could evidently change the wettability of substrate surfaces (Fig. 5b). The static contact angle of the substrates changed to 50°–70° after PDA coatings (Fig. 5c). AFM measurements of the PDA coatings on glass demonstrated that the thickness of PDA films was about 18 nm after 1 h ultrasound treatment (Fig. 5e), which typically needed 3 h to obtain the similar thickness if the ultrasound is absent [7]. The PDA thickness increased along with the increase of reaction time, which was 44 nm after 4 h ultrasound treatment (Fig. 5d), which was due to that free radicals generated by ultrasound promoted the formation of PDA and shortened the time to obtain the same thickness of films. The PDA coatings could also trigger the secondary reactions via Michael addition and/or Schiff base formation to graft functional molecules containing amine or thiol groups [7].

The elements and chemical bonds of PDA coatings on silicon wafers initiated by ultrasound were analyzed by XPS (Fig. 6). The
disappearance of the Si2p peak and the appearance of the N1s peak around 400 eV after coatings indicated the deposition of PDA (Fig. 6a and b). The Cls signal at 284.5 eV was attributed to the carbon in C–C, C–C, and C–H. The signal at 285.8 eV was attributed to the carbon in C–O and C–N, while the signal at 287.8 eV was attributed to the carbon in C–O (Fig. 6c). The appearance of C–O indicated that part of the phenolic hydroxyl group in PDA was oxidized to quinone. The O1s signal at 532.9 eV and the signal at 531.1 eV were attributed to the oxygen in O–H and C–O, respectively (Fig. 6e). The O1s signal also indicated the formation of quinone. The N1s signal at 399.1 eV and the signal at 531.1 eV were attributed to the nitrogen in C–N and N–H, respectively (Fig. 6d). The appearance of C–N and N–H indicated the formation of dopaminochrome (the cyclization product of dopamine quinone). The N1s signal showed the presence of RNH+, indicating cation–π interaction.
could be involved in the formation of PDA.

In addition, high frequency ultrasound could also generate PDA coatings in anoxic, neutral or acidic aqueous solutions (Fig. S3a–e). Hydrophobic polystyrene substrates after PDA deposition with or without the presence of ultrasound at pH 8.5 was rough and the contact angle was about 60° (Fig. S4), while the contact angle of the polystyrene substrate without PDA deposition was about 90° (Fig. 5c). From the AFM images, PDA coatings can be formed in anoxic dopamine solution at pH 8.5, 7.0, and 5.5 when high frequency ultrasound was applied (Fig. S3c–e). However, the substrate surface was smooth after incubation in anoxic dopamine solution regardless of solution pH (Fig. S3h–j). The static contact angle of the related substrates was about 90° similar to uncoated substrate (Fig. S4). Although the ultrasound-assisted PDA coatings formed in anoxic and acidic conditions were not dense enough, it could still change the wettability of the substrate (Fig. S4).

4. Conclusions

In summary, we reported a facile method to accelerate the oxidative polymerization of dopamine and PDA coatings on various substrates even in anoxic and acidic conditions. Compared with the conventional method, it takes less than 50% of coating time to obtain the same thickness of PDA films through sonopolymerization. Oxidizing radicals generated by high frequency ultrasound played a vital role in the oxidative polymerization of dopamine, where no additional oxidizing agent was required to be added during the whole process. In addition, it allows the control over the polymerization by turning the sonication on and off. The sono-assisted surface coating strategy is an environmentally friendly, cost-effective, and time-saving method for initiating and accelerating the polymerization of dopamine and PDA coatings on various surfaces.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ultsonch.2021.105571.

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