Preparation and properties of a pH-responsive PDMS platform

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Preparation and Properties of a pH-responsive PDMS Platform

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Abstract. In recent years, dopamine has attracted much attention as a surface modifier that can be widely used in biological, electrochemical and membrane applications. We herein report a pH-responsive polydimethylsiloxane (PDMS) platform modified with polydopamine nanospheres (PDA Ns). PDMS has excellent optical transparency and elasticity, good biocompatibility and good insulation. We prepared PDMS platform on microscope slides and grafted the polydopamine nanospheres to make it rough and obtained the superhydrophobic structure. The test shows the modified rough structure is stable and pH responsive.

Keywords: pH responsive, polydopamine, PDMS
PACS: GO4-382

INTRODUCTION

Mussels in the ocean can be easily adhered to almost all types of inorganic and organic substrates, including superhydrophobic and superhydrophilic substrates, with strong adhesion and good stability. It was found that 3,4-dihydroxy-L-phenylalanine (DOPA) and lysine-enriched proteins are the major source of particularly strong adhesion[1-4].

The structure of dopamine is similar to DOPA. In recent years, dopamine has attracted much attention as a surface modifier that can be widely used in biological, electrochemical and membrane applications. Polydopamine (PDA) can be obtained by oxidation of dopamine hydrochloride in alkaline aqueous solution (pH >7.5) with oxygen. Solution oxidation is the most common method to prepare polydopamine without complicated conditions and instruments. Changing the conditions of solution oxidation can produce different forms of polydopamine. For example, at room temperature, dopamine hydrochloride can be directly polymerized into well-dispersed polydopamine nanospheres (PDA Ns) in a mixture containing water, ethanol and ammonia without the help of templates. The size of PDA Ns can be adjusted by changing the concentration of ammonia[7].

Due to the good hydrophilicity of dopamine, the water contact angle of the surface modified by polydopamine deposition is generally in the range of 37-90 °. Polydopamine has rich functional groups such as catechol and imine. On the one hand, molecules containing nucleophilic groups such as amino or mercapto can react with polydopamine via Schiff base Reaction or Michael Addition. These reactions are mild and can happen generally be simply mixed at room temperature. On the other hand, the existence of different functional groups makes polydopamine a kind of amphoteric ion. Its isoelectric point is about 4, when pH value is lower than 4, the amine group in polydopamine will be protonated to make the polydopamine have positive charge, and when pH value is greater than 4, the phenolic group will deprotonize and make the polydopamine have negative charge[5].

We herein report a pH-responsive polydimethylsiloxane (PDMS) platform modified with polydopamine nanospheres (PDA Ns). PDMS has excellent optical transparency and elasticity, good biocompatibility and good insulation[6]. We prepared PDMS platform on microscope slides and grafted the polydopamine nanospheres to make it rough and the superhydrophobic structure was obtained. The modified rough structure is stable, the contact angle is pH responsive.

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EXPERIMENTAL

Materials

Dopamine hydrochloride, Cysteamine, 2,2-Dimethoxy-2-phenylacetophenone (DMPA)， Dow Corning 184 silicone elastomer, curing agent, microscope slides, Ammonia solution (28% in H_2O)， absolute ethanol were purchased from Aladdin Chemistry Co. Ltd, China.

Preparation of the pH-responsive PDMS Platform

Preparation of the PDMS platform: Cleaning glass slides in absolute ethanol for 15 minutes by ultrasonic and dry them with nitrogen. The PDMS substrates were prepared by mixing a silicone elastomer base with a curing agent in a weight ratio of 10 : 1. The mixture of 0.4 g was added to each glass slide, then flattened and placed in a vacuum oven at 70 ℃ for 1 hour to remove air bubbles and initially cured.

Preparation of a amino modified PDMS platform: 0.1 g β -mercaptoethylamine and 0. 005 g DMPA were dissolved in 25 ml absolute ethanol and then the PDMS platform was soaked in the intermixture for 1 minute and dry. Repeat 3 times, then react 30 minutes under ultraviolet light (365 nm). The unreacted substance was removed by washing with absolute ethanol and then dried and cured in a vacuum oven at 70 ℃.

Synthesis of polydopamine nanospheres with an average diameter of 300 nm: 0.4 mL ammonia aqueous solution was mixed with 7.5 mL ethanol and 18 mL deionized water under stirring at room temperature for 1 hour. 0.1 g Dopamine hydrochloride was dissolved in 5 mL deionized water and then injected into the mixture solution. The color of the mixture solution turned to pale yellow immediately and gradually changed to dark brown. After 24 h, the PDA Ns were obtained by centrifugation and washed with absolute ethanol for three times. polydopamine nanospheres with an average diameter of 200 nm were prepared by increasing the volume of ammonia aqueous solution to 0.6 mL.

0.05 g polydopamine nanospheres were dissolved in 25 ml deionized water, then the amino modified PDMS platform was putted in and stirred for 3 hours to obtain the PDMS platform modified by polydopamine nanospheres (PDMS-PDA Ns platform).

CHARACTERIZATION

The morphology of polydopamine nanospheres was tested by the typical scanning electron microscopy (SEM, VEGA3 TESCAN., Czech) and determination of particle size distribution of sample solution by zatasizernanozs high sensitivity dynamic light scattering instrument (NanoBrook Omni., USA) with scattering intensity measurement angle 90° at 25℃. Surface morphology and roughness measurements were conducted on a Veeco multimode III AFM (Veeco Instruments Inc., USA) in tapping mode. Water contact angles were recorded with OCA 15EC video-based optical contact angle measuring system (Eastern-Dataphy Instruments Co., Ltd., Beijing).

RESULTS AND DISCUSSION

As illustrated in Fig. 1a and Fig.1b , the typical scanning electron microscopy (SEM) imagings showed that the shape of PDA Ns were spherical. The size of the PDA Ns can be adjusted by changing the concentration of ammonia. As the Fig. 1c and Table 1 showed, here we got two kinds of PDA Ns with different average diameter of approximately 200 nm and 300 nm. Dynamic light scattering data indicated the polydispersity (PDI) of 200 nm and 300 nm PDA Ns were 0.031 and 0.067 respectively, which meant the PDA Ns had a stable size and a good dispersion.

TABLE a). DLS data of two sizes of PDA Ns

Sample ID	Eff. Diam. (nm)	Polydispersity
PDMS-200 nm PDA Ns	201.61	0.031
PDMS-300 nm PDA Ns	308.59	0.067

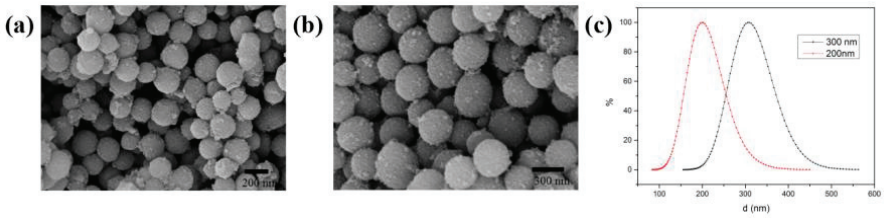

FIGURE 1. a) SEM image of PDA Ns with an average diameter of 200 nm. b) SEM image of PDA Ns with an average diameter of 300 nm. c) Particle size distribution graphic of PDA Ns

The microscopic morphology of PDMS-PDA Ns platforms were visualized and measured by the tapping-mode AFM (Fig. 2). Fig. 2a showed the surface of PDMS platform modified by 200 nm PDA Ns, which has uniform spherical protuberances, resulting in a RMS roughness value of 23.682 nm. As shown in Fig. 2b, the surface of PDMS platform modified by 300 nm PDA Ns also has uniform spherical protuberances, as indicated by the higher RMS roughness values of 73.397 nm. The PDMS plate modified with smaller particle size is relatively smoother. Due to the stacking of PDA Ns, the surface of PDMS platform is not smooth, which would cause super-hydrophobicity.

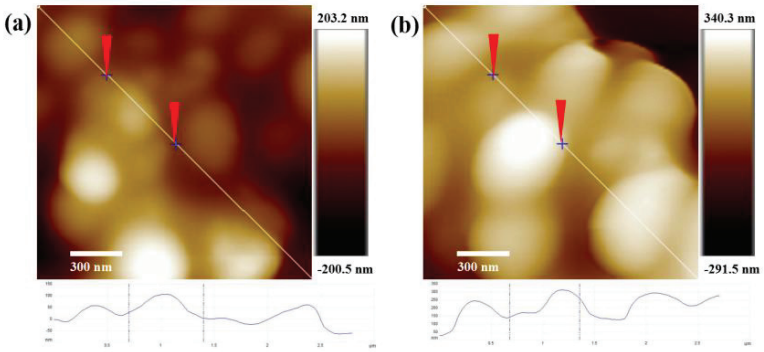

FIGURE 2. Tapping-mode AFM for (a) PDMS-200 nm PDA NS and (b) PDMS-300 nm PDA NS.

As shown in Fig. 3a and Fig. 3b, the surface of the modified PDMS is pH responsive and the change of contact angle can reach about 20° when pH is less than 4. The isoelectric point of polydopamine is pH 4 , so when pH is over 4, because of the existence of catechol structure, the phenolic hydroxyl group on polydopamine is easily oxidized to quinone structure by air, and only a few phenolic hydroxyl groups remain to form oxygen negative ions, that's why the hydrophilicity is not changed much. When pH is less than 4, the imine structure on the polydopamine binds to the hydrogen ion, and the catechol structure is preserved, so it becomes hydrophilic[5]. As can be seen from Figure 3b, the change of the contact angle of PDMS with different sizes of PDA Ns at different pH values is not significant. This is because the surface of the grafted PDA Ns has obtained the micro-structure, which has super hydrophobicity, and the pH responsiveness is mainly caused by the subamino and phenolic hydroxyl groups of the polydopamine. So the pH responsiveness of modified PDMS is almost irrelevant to the size of grafted PDA sphere.

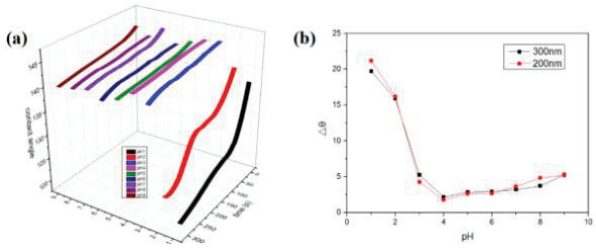

FIGURE 3. a) Change trend of water contact angle in 5 minutes at different pH. b) Variation of water contact angle in 5 minutes at different pH.

CONCLUSION

We herein report a pH-responsive polydimethylsiloxane (PDMS) platform modified with polydopamine nanospheres (PDA Ns). The modified PDMS surface has a micro-nano rough structure, which provides a good hydrophobicity. The change of water contact angle of the modified surface can reach about 20° under acidic conditions.

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