CuSO$_4$/H$_2$O$_2$-Induce Rapid Polymerization of Dopamine on Cotton Fabric for Oil/Water Separation

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Abstract: CuSO$_4$/H$_2$O$_2$ was used as the oxidation system to induce rapid polymerization of dopamine(DA) which modified the surface of cotton fabric. FTIR analysis showed that polydopamine(PDA) was successfully bonded to the surface of cotton fabric by DA self-polymerization under CuSO$_4$/H$_2$O$_2$ system. The surface of cotton fabric modified by PDA could change from hydrophilicity to hydrophobicity. Compared with traditional dopamine deposition, the cotton fabric modified by rapidly deposited PDA had better hydrophobicity, and which could apply for the oil/water separation. Through the test, the separation efficiencies of modified cotton fabric by rapidly deposited PDA all reached above 96% for three different types of oil/water mixture after three times, indicating that PDA modified cotton under CuSO$_4$/H$_2$O$_2$ condition for oil/water separation had good efficiency and reusability.

1. Introduction
Recently, there has been increasing interest in the mussel-inspired chemistry of dopamine(DA) for surface modification [1]. As an effective component of adhesive proteins in mussels, dopamine self-polymerization forms a polydopamine(PDA) coatings that can adhere to almost all substances. And PDA contains a variety of active groups such as o-diphenylquinone, pyrole, catechol and amino [2-4], so it can provide secondary reaction platforms for the matrix to form various functional layers[5].

The traditional polymerized deposition of DA generally has the problems of long deposition reaction time, poor uniformity and poor stability of coating[6], which greatly limits the large-scale application of PDA coatings. To solve the above problems, researchers used electrochemical drive, ultraviolet radiation or oxidant methods to induce rapid polymerization deposition of dopamine, which greatly has shortened the deposition time and improved the stability of the coating [7-8].

In this paper, dopamine was rapidly polymerized using CuSO$_4$/H$_2$O$_2$ as oxidant on cotton fabric surface for hydrophobic modification, and then modified cotton fabric applied for oil/water separation. Nowadays, a large amount of oily wastewater discharged in our daily life and industrial production has caused serious pollution and damage to the ecology and environment [9]. The study of an efficient oil/water separation material is of great importance to both industrial production and human life.

2. Materials and methods
2.1. Materials and reagents
Cotton plain cloth (18.45Tex*18.45Tex, 110 g/m²); Tris; Dopamine hydrochloride (98%); 30% Hydrogen peroxide; Copper sulfate pentahydrate; sodium hydroxide; concentrated hydrochloric acid; all the above reagents are AR grade.

2.2. Test instrument
HWS12 water bath thermostatic oscillator; STARTER2100 pH meter; BS210S automatic photoelectric balance; DZF-6053 vacuum drying oven; JC2000C contact Angle measuring instrument; The NEXUS-870 Fourier Infrared Spectrometer, Nicolet Instruments.

2.3. Experimental method

2.3.1. Cotton fabric pretreatment. Cotton fabric was treated by 20g/L sodium hydroxide solution at 100°C for 1h using a liquor ratio of 1:50, and then took it out and washed it repeatedly with deionized water. Repeated the above steps, and then dried it for later use.

2.3.2. Preparation of cotton fabric modified by dopamine. A certain amount of dopamine hydrochloride was dissolved in 50mL tris-HCl buffer solution (pH=8.5, 50mM). In case of rapid deposition, CuSO4 and H2O2 oxidation system should be added later for rapid stirring till dissolution. The pretreated cotton fabric was rapidly immersed in dopamine hydrochloride-Tris buffer solution at a bath ratio of 1:30, and reacted in a water bath thermostatic oscillator (with a vibration frequency of 80 times/min) at room temperature for a period of time. After being removed, it was fully washed with deionized water, and then placed in an oven at 60°C for 2h to dry.

2.4. Testing methods

2.4.1. Infrared Spectroscopy. Fourier transform infrared spectrometer was used to measure the surface attenuation and total reflection of cotton fabric before and after modification to observe the changes of the surface groups.

2.4.2. Fabric Contact Angle Test. The contact Angle was measured by projecting the trace liquid drops onto the surface of fabric through the contact Angle tester. Each sample was measured three times and the average value was taken.

2.4.3. Testing of fabric oil-water separation performance. A little Sudan III was added into oil, and then oil showed red. According to the experimental amount, different proportions and different types of oil were taken and mixed with water to make oil/water mixture. The experimental cotton fabric was folded twice in half and kept close to the edge of the funnel without cracks, then oil/water separation test was carried out. The calculation formula of oil-water separation efficiency (R, %) is as follows:

\[ R (\%) = \frac{V_2}{V_1} \times 100 \]

Where: The \( V_1 \) is the volume of the initial oil and the \( V_2 \) is the volume of the separated oil.

3. Results and discussion

3.1. Characterization of dopamine-modified cotton fabric by CuSO4 / H2O2 rapid polymerization
Figure.1 Schematic diagram of rapid polymerization of dopamine on cotton fiber surface

Figure.1 shows the reaction process of dopamine rapid polymerization and deposition under CuSO$_4$/H$_2$O$_2$ system. Using CuSO$_4$/H$_2$O$_2$ system in alkaline medium can generate a large amount of active oxygen free radicals (OH, HO$_2^-$ and O$_2^{2-}$) [10], which can induce dopamine oxidation quickly to produce dopamine quinone compounds with quinone structure. And then disproportionation reaction can take place between the two to obtain dopamine with semi quinone and semi free-radical structure. Finally, through the coupling reaction of free radicals of dopamine molecule links, dense adhesion polymerization of polydopamine are coated on the cotton fabric. Besides, Cu$^{2+}$ can further increase the crosslinking degree of the PDA coating through the coordination bond[6].

Figure.2 FT-IR of cotton fabric before and after modification

Figure.2 shows the infrared spectra of cotton fabric before and after PDA modification under CuSO$_4$/H$_2$O$_2$ system. It can be seen that compared with the original cotton, spectra of modified cotton showed a more obvious absorption peak at 1586 cm$^{-1}$, which was considered as the characteristic peak of indole structure produced during the self-polymerization assembly of dopamine. And the peak strength of modified cotton fabric was enhanced at 2842 cm$^{-1}$, which was assigned to the stretching vibration peak of methylene C-H of PDA molecule [11]. In addition, PDA modified cotton showed a new absorption peak at 1737 cm$^{-1}$, which was mainly caused by the formation of polydopamine molecule containing carbonyl structure. These results demonstrate that dopamine was successfully attached to the surface of cotton fabric by self-polymerization deposition under the oxidization system.

3.2. Analysis of hydrophobic properties of modified cotton fabric

(a) original cotton  (b) PDA modified  (c) PDA modified PET triggered by CuSO$_4$/H$_2$O$_2$
Figure.3 Hydrophobic effect and contact angle test of cotton fabric before and after modification

Figure.3 shows the hydrophobic effect and the static water contact Angle test photos of cotton fabric under different conditions. It can be seen that the original cotton fabric had good hydrophilicity with a contact angle of 18°, and water droplets quickly infiltrated into its surface when dripping. Compared to Figure 3(a), (b) and (c), the surface of cotton fabric modified by PDA changed from the original hydrophilicity to hydrophobicity. The contact angle of PDA modified cotton fabric by traditional air oxidation deposition (24 h) was 102°, while PDA modified cotton fabric by CuSO₄/H₂O₂ rapidly deposition (1h) was 133.5°. The results indicated CuSO₄/H₂O₂ could enhance the hydrophobicity of modified cotton fabric.

3.3. Effect of CuSO₄ concentration on the contact angle of PDA modified cotton fabric

As shown in Figure 4, after rapid polymerization of DA on the surface of cotton fabric at different CuSO₄ concentration (3, 5, 7, 9, 12 mM), the contact angle of cotton was over 100° and its surface became hydrophobic. Meanwhile, the contact angle of modified cotton fabric increased constantly with the increasing of CuSO₄ concentration, and the contact angle rose to 145° at 9 mM CuSO₄. This is mainly because the polar groups of PDA are hydrogen bonded to cellulose and coordinated with Cu²⁺, leaving its hydrophobic group exposed to the surface of cotton fibre. However, its contact angle decreased slightly when increasing the CuSO₄ concentration above 9 mM. Therefore, PDA modified cotton at 9 mM CuSO₄ was chosen for next oil/water separation experiments.

3.4. Oil-water separation experiment of modified cotton fabric

3.4.1. Oil-water separation effect of cotton fabric before and after modification. PDA modified cotton fabric was used to separate the oil from water. Vegetable oil added with a little Sudan dye turned red while water was still colourless. It can be observed from Figure.5 that when the original cotton was used for the separation experiment of vegetable oil/water mixture, the oil/water mixture flowed along the wall of the funnel in a column and the cotton fabric had no separation effect on the oil/water mixture. However, for the cotton treated with CuSO₄/H₂O₂ rapidly polymerized dopamine, only the vegetable oil of the mixture flowed down the funnel wall and the water stayed on the surface of the dopamine-modified cotton fabric, indicating that PDA modified cotton fabric had good separation effect on the vegetable oil/water mixture.
3.4.2. Different kinds of oil-water separation effect. Vegetable oil, mineral oil and dimethyl silicone oil were used to prepare oil/water (20:5) mixture respectively, and oil/water separation experiments were conducted for three times. The experimental datas are shown in Figure.6.

As shown in Figure.6, with the increase of separation times, the oil/water separation efficiencies were all gradually improved, which may be due to part of oil adsorbed on the surface of modified cotton fabric and further enhanced its water-repellent property. PDA modified cotton fabric had high separation efficiency for different types of oil/water mixtures after 3 times. The highest separation efficiency of modified cotton fabric for mineral oil was nearly 100%, followed by the separation efficiency of vegetable oil and dimethyl silicone oil which separation efficiency also reached over 96%. The above results indicated that the modified cotton fabric had higher reusability and universal applicability for oil/water separation.

4. Conclusions
Polymerized depositon of DA on the surface of cotton fabric can change the wettability of the fabric. Compared with air oxidation deposition, PDA modified cotton fabric by CuSO$_4$/H$_2$O$_2$ rapidly deposition had better hydrophobicity, and of which the contact angle reached to 145° at 9 mM CuSO$_4$. For different types of oil/water mixture (vegetable oil, mineral oil and dimethyl silicone oil), modified cotton fabric by rapidly deposited PDA all had good separation efficiency and durability.

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