Temperature-controlled 3-phase oil-water-oil continuous separation by PNIPAM-modified stainless steel mesh

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Abstract. In recent years, the frequent occurrence of oil spills has been a serious threat to marine and aquatic ecosystems. The environmental and economic demands also emphasize the need for materials which can effectively separate oil and water. In order to handle these environmental issues caused by oil spills, all kinds of oil-water separation methods have been developed. In this work, we have fabricated a thermosensitive device with a simple and versatile method: we sprayed the spray adhesive onto a stainless steel mesh box, then amino-P25 nanoparticles were sprayed onto the device directly. Finally, PNIPAM was synthesized on the surface of device. The wettability of PNIPAM modified separation device can be controlled by temperature and finally a 3-phase oil-water-oil continuous separation was realized.

1. Introduction

The smart material with conversion of wettability on external stimuli has attracted widely attention because of their promising potential in fabricating intelligent controllable materials. [1-5] These smart responsive materials can display controlled changes in response to physical or chemical changes of the external environment, such as temperature, pH, light, electricity, and magnetism. [6-12] The smart responsive materials have numerous applications in many fields, for example, in biomedical field, light-, pH-, and temperature-responsive dendrimer systems with different chemical compositions and architecture can be used to encapsulate and release drugs. In the meantime, they also have potential application in many other fields such as sensors, enzyme immobilization, and changing wettability. For example, some typical smart responsive materials are utilized to fabricate responsive surfaces with reversibly switchable wettability to realize oil-water separation.

In recent years, the frequent occurrence of oil spills has been a serious threat to marine and aquatic ecosystems. The environmental and economic demands also emphasize the need for materials which can effectively separate oil and water. In order to handle these environmental issues caused by oil spills, all kinds of oil-water separation methods have been developed to recover spilt oil from marine environments, such as physical diffusion, bioremediation13, 14, oil skimmers[15] and so on. Owing to the difference of interfacial effects for oil and water, utilizing the wetting behavior of solid surfaces to design an oil-water separating material has attracted a great deal of attention in fundamental research and for potential application in the field of oil-water separation.

In this work, we utilized stainless steel mesh as a substrate, spray adhesive was sprayed on the substrate directly. Following, amino-P25 nanoparticles were dispersed in absolute ethanol forming a

paint-like solution and then sprayed onto the adhesive coated substrate directly. Finally, poly (N-isopropyl acrylamide) (PNIPAM) was generated on the surface of amino-P25 coated substrate. Consequently, thermosensitive surface that can change from super hydrophilic to super hydrophobic by heating was obtained and used in 3-phase oil-water-oil separation.

2. Experimental

2.1. Materials and Instruments

Oil Black and Scarlet 4GE (Askul Co., Ltd., Japan), Stainless steel mesh (Anping Huirui Wire Mesh Manufacture Co., Ltd., China), Spray adhesive (Sumitomo3M Co., Ltd., Japan). Toluene, ethanol, dichloromethane, methyl, APTES, N-isopropyl acrylamide and trimethylamine were purchased from Nacalai tesque. 2-Bromo-2-methyl-propionyl bromide, CuBr and PMDETA were purchased from Sigma Aldrich. All chemicals were analytical grade reagents and were used as received.

Scanning electron microscopy (SEM) measurements were carried out on an EVO MA 25 instrument at 20.0 kV. Photographic images were taken with a Nikon camera (D5000).

2.2. Fabrication of the Amino-P25 Coated Stainless Steel Mesh

P25 nanoparticles and 10%wt APTES was added into absolute ethanol and refluxing for 12h, then the amino-P25 nanoparticles were vacuum dried for 12h under 60 ºC. Stainless steel mesh was folded into an open and rectangular box with an edge length of 3 cm×3 cm×1 cm. The as-prepared box was ultra-sonicated in ethanol and deionized water for three times, and dried in oven. Spray adhesive was sprayed onto the box directly, following, amino-P25 nanoparticles were dispersed in absolute ethanol forming a paint-like solution and then sprayed onto the adhesive coated substrate directly.

2.3. Synthesis of the PNIPAM Coating

400 μL trimethylamine was added into 20 ml dichloromethane and stirred for 30 min, and then the amino-P25 coated box was put into the solution, following, 1 ml of 2-Bromo-2-methyl-propionyl bromide was added and stirred for 1h. Finally, the treated as-prepared stainless steel box was take out and washed for 3 times with deionised water.

For the synthesis of PNIPAM coating on the as-prepared box, as-prepared box was added into a mixture of 20 ml methyl and 20 ml deionized water. Then, 1.6 g N-isopropyl acrylamide and 25 mg CuBr was added into the solution and stirred. Finally, 560 μL PMDETA was added and stayed for 1 h under 60 ºC. After wash and drying, a thermosensitive oil-water separation device was obtained.

2.4. Oil-Water-Oil 3-Phase Separation

In order to distinguish oil phase and water phase from oil-water-oil mixture, we dyed the dichloromethane layer with Solvent Black and toluene layer with Solvent Red to indicate the directional delivery. The labeled dichloromethane (5 mL) and toluene (5 mL) were added into a pipette with 5 mL of deionised water forming a stratified oil-water-oil mixture solution. After the as-prepared box put on the top of the supporting beaker, the mixture solution was discharged slowly. In the meantime, environment temperature was controlled to match up the separation process. Consequently, oil phase and water phase were separated.

3. Results and Discussion

3.1. Surface Modification and Characterization

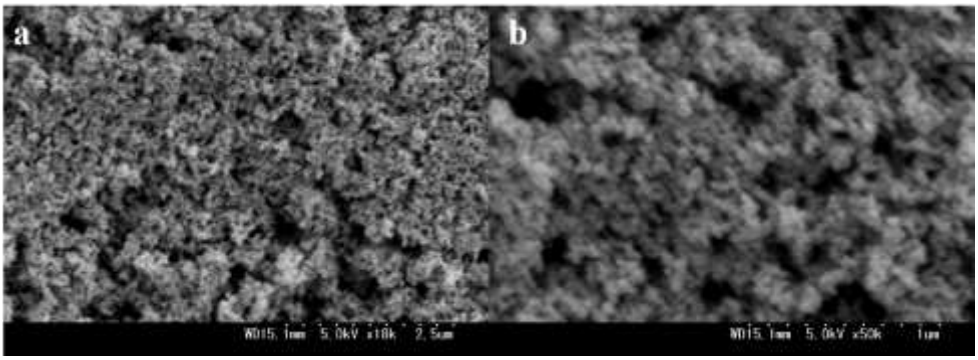

Figure 1. SEM images of the amino-P25 nanoparticles.

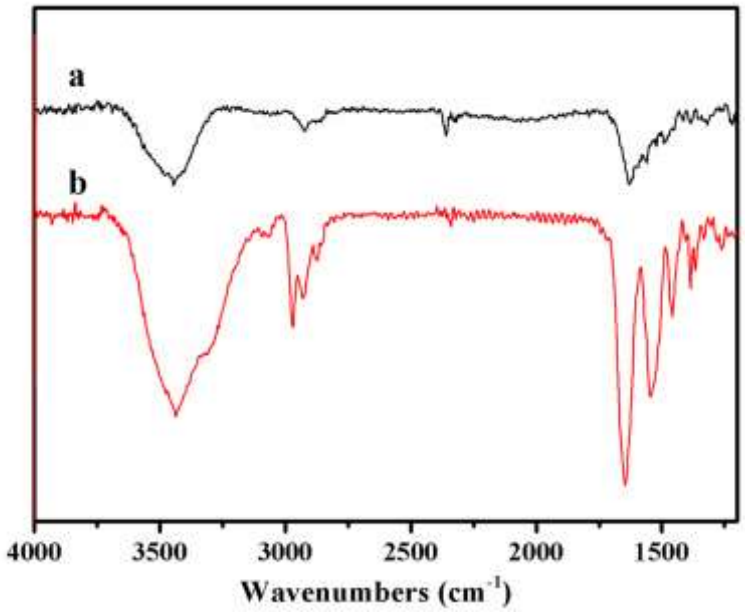

Figure 2. FT-IR spectra of the surface before (a) and after (b) generation of PNIPAM.

During modification, evident changes in wettability of the surface occurred in the process of preparing the thermosensitive oil-water separation device. After being coated by amino-P25 nanoparticle, the surface showed superhydrophilicity. As can be seen from figure 1, the amino-P25 nanoparticle showed an average particle size of 20 nm. In the meantime, as we can see from the figure 2, the FT-IR spectra of the device surface after generation of PNIPAM showed four obvious strong peaks from about 1380 cm^{-1} to about 1650 cm^{-1}. These four peaks belonged to the amido bond between PNIPAM and substrate which indicated PNIPAM has generated on the substrate surface successfully.

When the PNIPAM was generated on the surface of amino-P25 nanoparticles, the surface wettability emerged a temperature-responsive property. When temperature was higher than 37 ºC, the device surface showed superhydrophobicity, otherwise, the surface showed superhydrophilicity. Take advantages of this phenomenon, we designed a simple separation process to separate a 3-phase oil-water-oil mixture continuously.

3.2. 3-Phase Oil-Water-Oil Separation

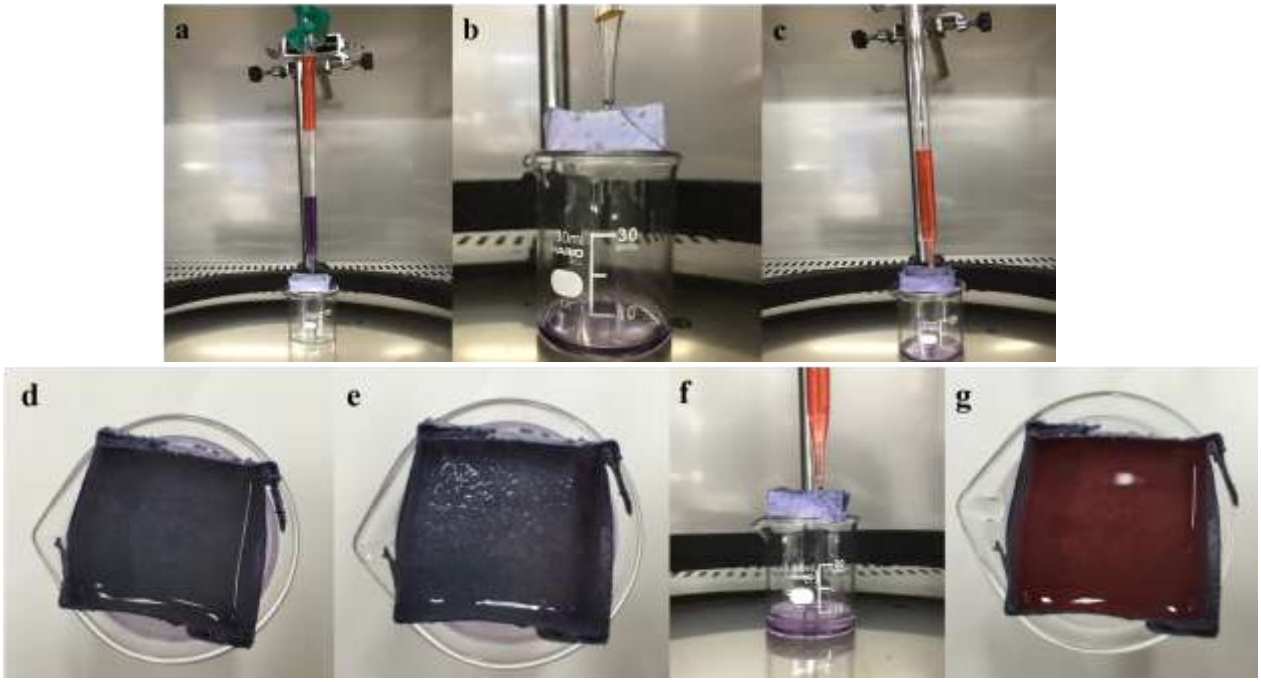

Figure 3. A 3-phase oil-water-oil separation process using the thermosensitive device.

We dyed the dichloromethane layer with Solvent Black and toluene layer with Solvent Red to indicate the directional delivery and distinguish oil phase and water phase from oil-water-oil mixture. In order to separate the oil phase and water phase continuously and respectively, the body temperature of temperature-responsive separation device was regulated through controlling environment temperature. As can be seen from figure 3a, we began the separation process above 37 ºC, thus the device surface was superhydrophobic. When dichloromethane dropped into the device, it was immediately taken up by the device, penetrated through the modified mesh, and finally dropped into the flask (figure 3b). Following, the water was dropped into the device (figure 3c), because of the superhydrophobicity, water was retained in the device (figure 3d). Next, we regulated the body temperature of device below 37 ºC, thus the wettability of device surface transformed into superhydrophilicity. As a result, the remained water penetrated through the device rapidly (figure 3e) and dropped into the flask. Finally, the red dyed toluene was dropped into the device (figure 3f). Because the device surface has transformed into superhydrophilic, the toluene was retained in device (figure 3g). Thereby, the 3-phase oil-water-oil continuous separation has been realized.

4. Conclusion

In this work, we have fabricated a thermosensitive device with a simple and versatile method: we sprayed the spray adhesive onto a stainless steel mesh box, then amino-P25 nanoparticles were sprayed onto the device directly. Finally, PNIPAM was synthesized on the surface of device. The wettability of PNIPAM modified separation device can be controlled by temperature and finally a 3-phase oil-water-oil continuous separation was realized.

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