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Communication

Simple fabrication of superhydrophobic PLA with honeycomb-like structures for high-efficiency oil-water separation

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ABSTRACT

Polylactic acid (PLA) is one of the most suitable candidates for environmental pollution treatment because of its biodegradability which will not cause secondary pollution to the environment after application. However, there is still a lack of a green and facile way to prepare PLA oil-water separation materials. In this work, a water-assisted thermally induced phase separation method for the preparation of superhydrophobic PLA oil-water separation material with honeycomb-like structures is reported. The PLA material shows great ability in application and could adsorb 27.3 times oil to its own weight. In addition, it could also be applicated as a filter with excellent efficiency (50.9 $m^3 m^{-2} h^{-1}$).

Nowadays, the water pollution caused by leaked oil and organic-compounds has caused serious negative impact on both ecological environment and economic development. In January 2018, an oil spill accident caused by a tanker collision occurred in Shanghai. 138,000 tons of oil was leaked and polluted a large area of the sea. Facing these challenges, oil adsorbents with special (super)hydrophobicity have attracted the attention from both academia and industry, for instance, metal meshes [1–3], sponges/foams [4–7], polyethylene bundles [8,9], and membrane [10–13]. However, the current research work mainly has the following three problems. Initially, the complicated and costly fabrication process of these material could be a barrier to the large-scale production. What's more, large amount of non-degradable raw materials will bring serious secondary pollution after large-scale adhibition. Last but not least, many non-renewable resources are heavily adopted. Here we should design a simple method to prepare environmentally friendly oil-water separation materials.

Polylactic acid (PLA), a bio-based and biodegradable material, origin from plant resources such as corn and cassava, which has attracted huge attention from researchers due to its great potential in vast applications [14]. In addition, due to its superior overall performance, porous PLA material is expected to be applicate in the field of oil-separation materials. However, to our knowledge, there are very few related studies on hydrophobic porous PLA materials in the open literature.

Thermally induced phase separation, a low-cast and template-free method to form polymer foam, has caused widespread interest among researchers. Unfortunately, similar with some extruded or injection-molded polymer materials, it owns a pellicle structure [15–18], the pellicle without porous structure will lead to the decrease of the separation ability. In this work, we greatly optimized this method by adding few drops of deionized water to prepare a superhydrophobic porous material. In this sturdy, the morphology of the porous material could be easily controlled. As a porous material composed with pure eco-friendly PLA, its excellent superhydrophobicity and oil adsorption efficiency could maintain after cycles of applications, which could be used to deal with large-scale crude oil spill accidents.

The deionized water (4 mL) was added in the solution of PLA and dioxane (2.5 g PLA per 100 mL dioxane) under high speed stirring. The obtained mixture was poured into petri dishes with an

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inner diameter of 75 mm and kept in a refrigerator below −4 °C for 12 h. Then, the sample was placed in a lyophilizer below −80 °C for 72 h at 10 Pa. For comparison, PLA without the addition of deionized water was also prepared by the same method. The PLA samples without and with water 2, 3 and 4 mL are called P0, P2, P3 and P4, respectively. Fig. 1a shows the fabrication process of superhydrophobic porous PLA. The surface of the P4 shows superhydrophobicity with a water (dyed with potassium permanganate) contact angle of 158°, and the cyclohexane (dyed with Sudan 3) droplets are fully adsorbed by the material with a contact angle 0°. In addition, sublimated dioxane ice crystals can be collected and reused during actual processing. Therefore, this low-cost green method can be applied in oil spill accidents on a large scale.

Interconnected porous structures give a path for gas content in and out of the material. As shown in Fig. 1b, the isotherm of P4 is typical IV which confirms the existence of mesoporous structure in the PLA material [7]. Additionally, according to the pore size distribution curve, there are many nano-level porous structure inside the material, indicating the increasing of specific area. The specific area of P0 and P4 are 80.34 m^2/g and 94.6 m^2/g, respectively.

The additional water could dramatically change the surface microtopography of the material. Fig. 2 shows the SEM images of P0 and P4. During the fabrication process, the deionized water could perform as an additional pore agent in the PLA/dioxane solution. The Flory-Huggins interaction parameter (χ) of the PLA/dioxane/water solution could be defined as follows:

$$\chi_{ij} = \frac{V_r(\delta_{PLA} + \delta_m)^2}{RT} \quad (1)$$

where V_r represents the molar volume of the mixed solvent (68.6 mL/mol); δ represents the solubility parameters, δ_{PLA} is 20 $(J/mL)^{1/2}$ and δ_m is 22.261 $(J/mL)^{1/2}$; the gas constant (R) is 8.314 J mol^{-1} K^{-1}; and T is the temperature (298.15 K). At room temperature, the χ between PLA and the mixture is 0.141. The result shows that the additional water will not cause phase separation before next operation [7,19]. Therefore, the special structure for P4 was

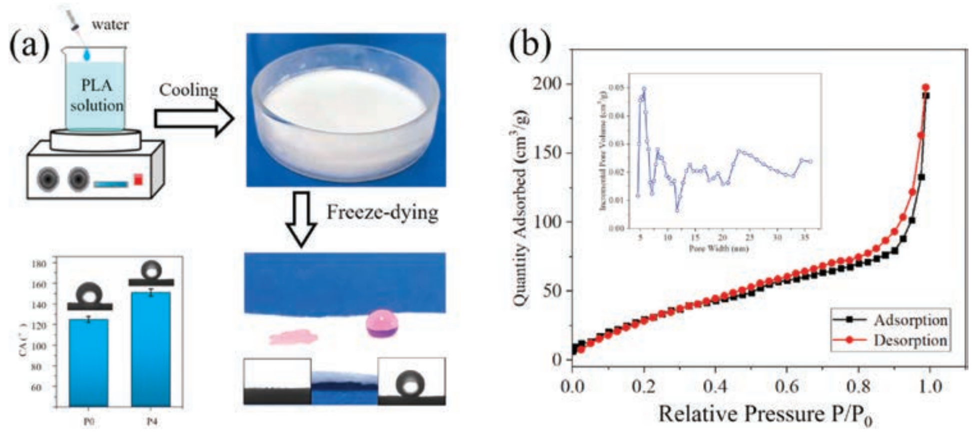


Fig. 1. (a) The fabrication process and the sample's oil and water contact angles. (b) Nitrogen adsorption-desorption isotherm and (insert) pore size distribution plot of P4.

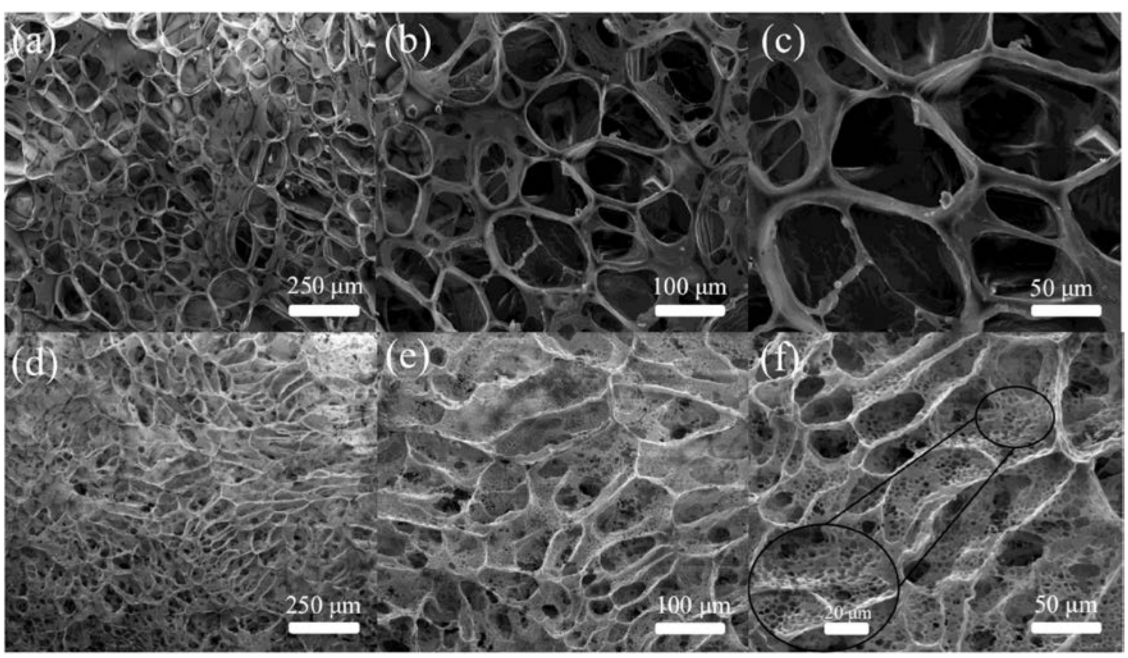
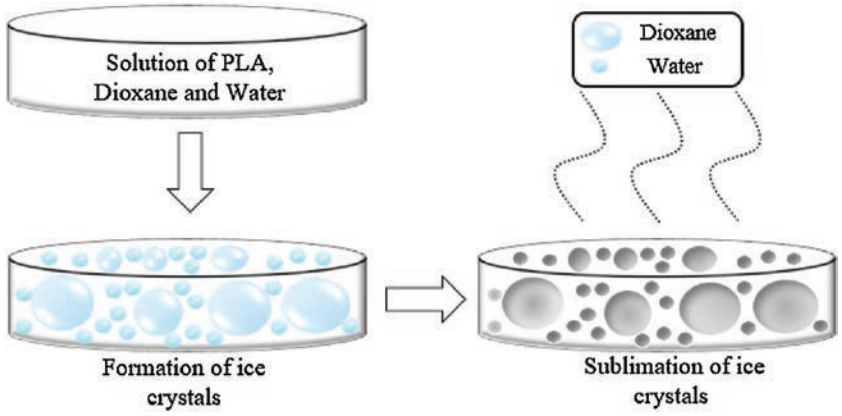


Fig. 2. SEM images of (a–c) P0 and (d–e) P4 surfaces.



Scheme 1. Formation of the porous structure of PLA material with the addition of water.

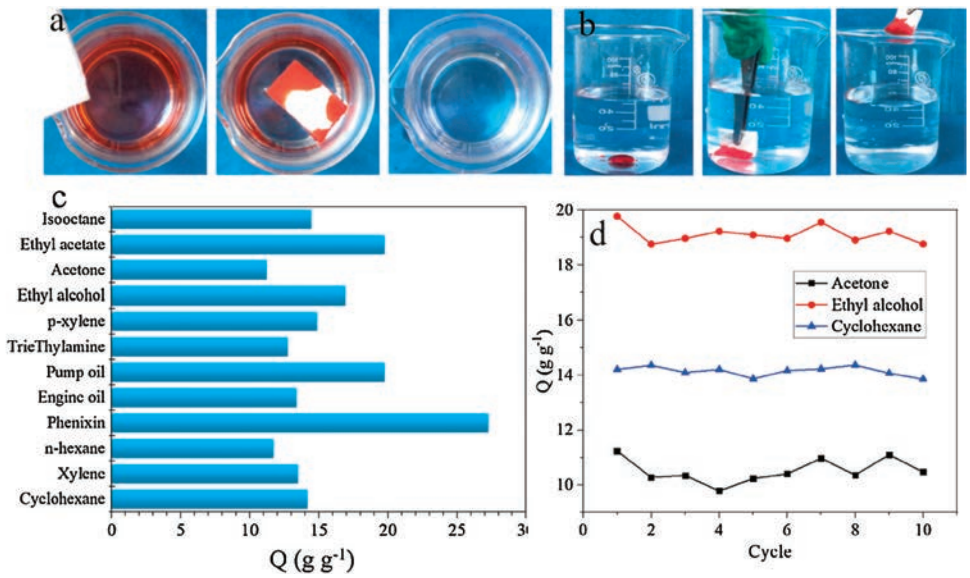


Fig. 3. Removal process of (a) the cyclohexane on surface of the water and (b) carbon tetrachloride under water. (c) The oil adsorption capacity of different oils and organic solvents. (d) Oil-absorption recycle ability in absorption/evaporation cycles.

formed through phase separation which occurs when the samples was kept in a refrigerator below −4 °C for 12 h. At this temperature, dioxane will form ice crystals (Scheme 1). Meanwhile, phase separation will take place between dioxane and PLA. The PLA will precipitate out of solution, producing a cell wall that surrounds the dioxane crystals [20]. The additional water will also precipitate from the dioxane, and form small ice crystals [6]. At the freeze-drying process, all the ice crystals were sublimated, leaving a porous PLA material ready for use. As shown in Figs. 2a–c, only micron-sized porous structure was observed on the surface of P0. As for P4, due to the introduction of water droplets, a large number of nano-scale pores appear on the cell wall of P4, which give the material a micro/nano hybrid honeycomb-like structure. These pores can form an air cushion, which will greatly improve the hydrophobicity of the PLA [21]. Therefore, it is expected to absorb spilled oil from water due to its outstanding hydrophobicity.

Because of the superhydrophobicity and large surface area of P4. We can foresee that the P4 could selectively adsorb oil and organic solvent from water. Figs. 3a and b show the P4 cleaning floating oil pollution (cyclohexane dyed with Sudan 3) and underwater oil pollution (tetrachloromethane dyed with Sudan 3). The oil pollution is completely absorbed leaving a cleaning water body. This shows that P4 could be applicated in cleaning large-scale leaked oil accident.

The amount of P4 adsorbed on different oils and organic solvents is shown in the Fig. 3c. The capacity of PLA material could absorb 11–26 times to its own weight. This huge capacity is higher than that of ordinary oil-water separation materials (Table S1 in Supporting information). This is because the special porous structure of PLA material, which give it the ability to hold more oil or organic solvent inside [7]. As for the recycle ability, the capacity of the material does not change obviously within ten cycles (Fig. 3d), showing great recycle ability.

The P4 could also be applicated for the flirtation in oil-water separation due to its hydrophobicity [3]. As shown in Fig. 4a, PLA material could block water columns with a height of 10 cm. A mixture contains of water and oil is poured into the separation setup; the oil quickly passed through the filter element, while the water is blocked and fail to pass (Fig. 4b). No passed water could be observed in the whole process. The maximum pressure of

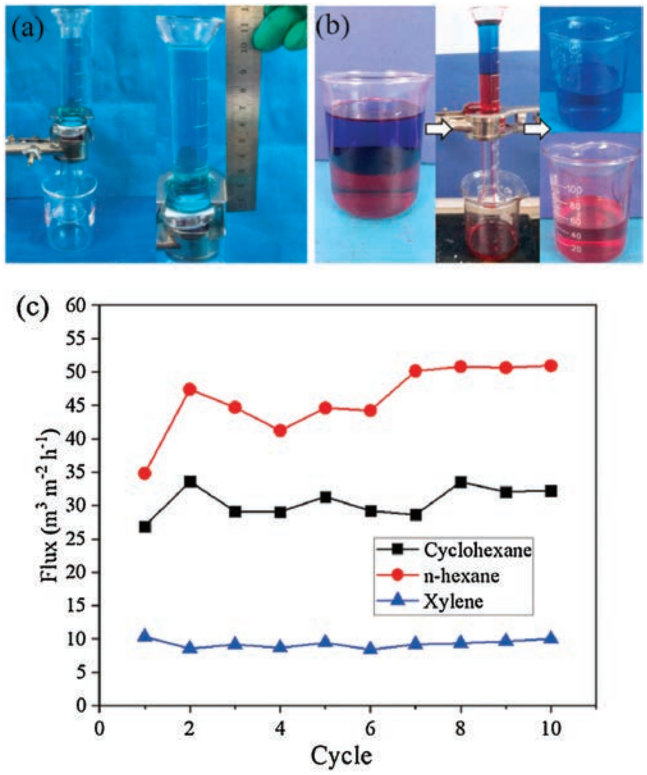


Fig. 4. (a) Water block ability and (b) photograph of hexane/water separation as well as (c) the recycled separation fluxes of different solvent mixture passing through P4.

cyclohexane, *n*-hexane and xylene is 305.69 Pa, 258.05 Pa and 341.42 Pa, respectively. In order to verify the oil-water separation efficiency of the material, flux was proposed which could shows the speed of the oil through the setup. In addition, during the separation process, the flux of P4 remains stable for 10 cycles (Fig. 4c), showing good recyclability.

In summary, a water-assisted thermally induced phase separation strategy is developed for the fabrication of an eco-friendly PLA material with special rough with honeycomb-like structures. The material could be applicated as an oil adsorbent and in gravity driven oil-water separation with high efficiency and recycle ability which will lead a way to achieving high-efficiency cleaning of large-scale leaked oil pollution.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.cclet.2019.07.044.

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