## Article

# Biodegradable PLA Non-woven Fabric with Controllable Wettability for Efficient Water Purification and Photo-catalysis Degradation

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# Biodegradable PLA Non-woven Fabric with Controllable Wettability for Efficient Water Purification and Photo-catalysis Degradation

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**KEYWORDS:** Biodegradable, PLA Non-woven Fabric, Controllable Wettability, Oil Absorption, Oil/Water Separation, Photocatalyst

**ABSTRACT:** Although many bio-inspired super-wetting materials with excellent capability for oil/water separation have been constructed, functional surfaces combining effective separation property, biodegradability and easy-controllability are still highly desired. In this work, a facile strategy to realize the controllable wettability on the polylactic acid (PLA) non-woven fabric has

been developed, the resulting super-wetting PLA non-woven fabrics exhibit high absorption capacity and high selectivity in oil/water separation. Moreover, the superhydrophilic PLA nonwoven fabric possesses excellent simultaneous photo-catalysis degradation of water-miscible toxic organic pollutants. With the versatility and biodegradability, these advanced PLA nonwoven fabrics may provide effective solutions to oily water treatment.

**INTRODUCTION**

Nowadays, the increasing industrial discharge of organic pollutants has caused tremendous threats to ecosystem, so the purification of oily wastewater has become a worldwide challenging task[1-3]. Therefore, it is highly desirable to develop advanced separation materials with high selectivity and efficiency[4-5]. Recently, much attention has been paid to bio-inspired super-wetting materials with excellent capability for oil/water separation. For instance, superhydrophobic materials in combination with surface chemistry and roughness, such as metal meshes[6], films[7-8], aerogel[9-10], sponges[11-14,] textiles[15-17], which can selectively separate oil from oily waste water. We have developed carbon nanotubes hybrid membranes for effective water/oil emulsions separation[18-19]. Superhydrophilic materials can separate water from oil, and simultaneously avoid the oily contamination of materials induced by permeated oils[20-24]. Materials with switchable wettability can selectively make water and oil permeate through orderly by adjusting various stimuli[25-28]. Although many efforts have been devoted to construct super-wetting separation materials for wastewater treatment, the post-processing of these used materials is still a daunting task because of their non-degradable essence. Conventionally, the polluted separation materials are directly discarded or burnt, inevitably giving rise to the secondary pollution to the ecosystem.

Polylactic acid (PLA) has been regarded as the most promising eco-friendly materials and is also expected to be developed into novel biodegradable separation materials. Feng et al. has prepared PLA films created by a non-solvent induced phase separation process for oil/water separation[29]. We have reported the functionalization of PLA non-woven fabric as superhydrophobic material for efficient oil/water separation[30]. Despite the progress, water pollution has presented particularly serious due to the presence of variety of soluble organic pollutants, the resulting water phase is not appropriate to drain into water system even after oil/water separation[31-32]. Therefore, from these perspectives, new functional surfaces possessing versatility, biodegradability and easy-controllability to realize the effective treatment of sewage sludge and organic waste water are highly anticipated.

Very recently, we have also constructed a serial of CNTs hybrid membranes for oil/water emulsion separation, accompanied with catalytic degradation of soluble organic molecules or antibacterial function[33-34]. Herein, based on the above concepts, we report a novel strategy to realize the controllable wettability on the porous PLA non-woven fabric for efficient water purification and photo-catalysis degradation. The schematic fabrication process is illustrated in **Figure 1**. Dopamine, a biomimetic molecule inspired by mussel adhesive proteins that contains catechol and amine groups, which can self-polymerize in an alkaline environment based on the aerobic auto-oxidatione[35-36], was used to modify PLA non-woven fabric to obtain polydopamine (PDA)/PLA non-woven fabric (**Figure 1A**). The advanced PLA non-woven fabric was then fabricated by controlling the relative proportion of butyl titanate ($Ti(OBu)_4$) and heptadecafluorononanoic acid (HFA). When the proportion of HFA and $Ti(OBu)_4$ is higher, the non-woven fabric is superhydrophobic, inversely, with lower proportion of HFA and $Ti(OBu)_4$, the obtained fabric is superhydrophilic (**Figure 1B, 1C**). Both of them could separate oil/water

mixtures efficiently. More interestingly, the superhydrophilic PLA non-woven fabric has

excellent photo-catalysis degradation property for various soluble organic pollutants, which

holds possible applications in environmental cleanup and self-cleaning. All in above, this work

provides a new pathway to fabricate oil/water separation materials with both versatility and

biodegradability, which shows attractive potential applications in water purification.
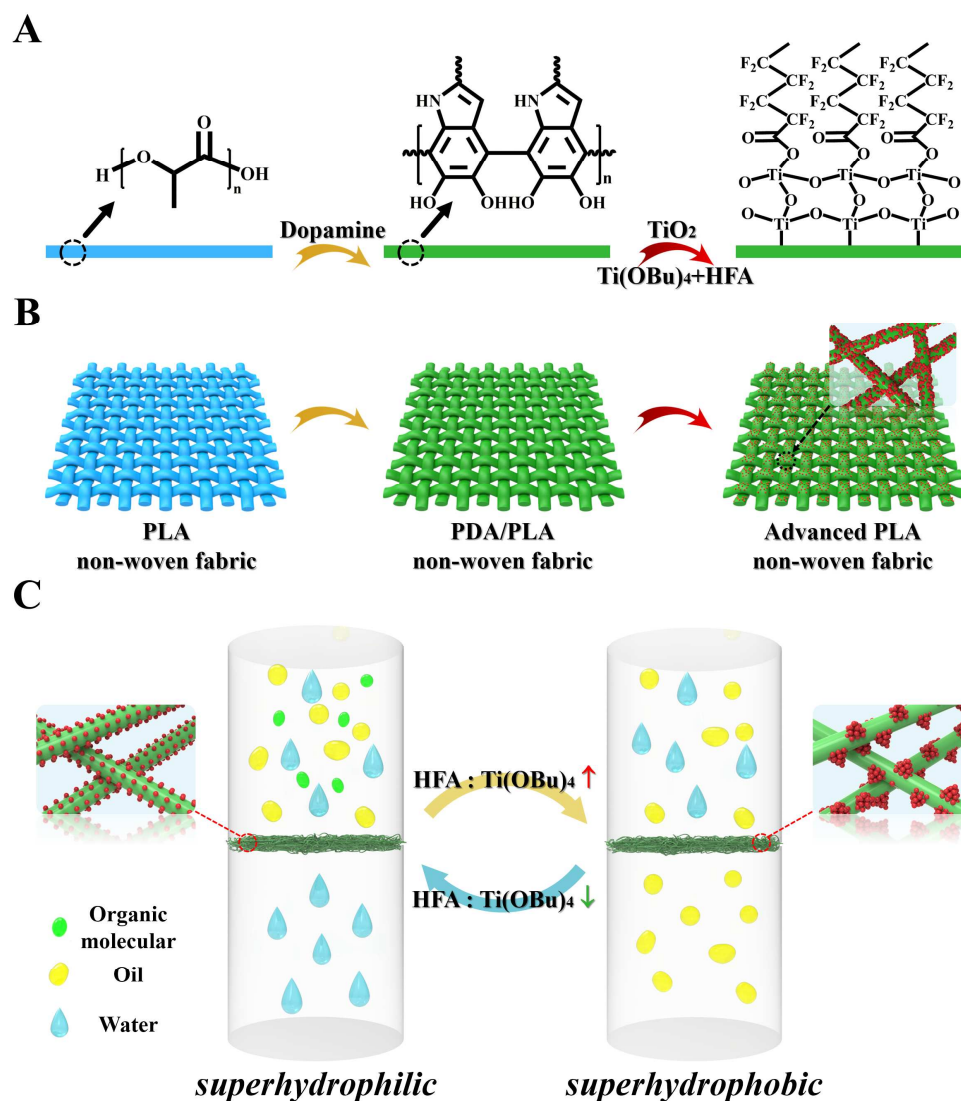


**Figure 1.** Schematic illustration of the preparation of the advanced PLA non-woven fabric for oil/water separation. (A, B) The advanced PLA non-woven fabric was modified with PDA and $TiO_2$ nanoparticles. (C) The wettability was adjusted according to the relative proportion of $Ti(OBu)_4$ and HFA, and the obtained fabrics were applied in oil/water separation, respectively.

**EXPERIMENTAL SECTION**

**Materials:** The raw PLA non-woven fabric (diameter 20-25 μm) was purchased from Zhejiang Hisun Biomaterials Co., Ltd, which was rinsed thoroughly with anhydrous ethanol, dried in a stream of nitrogen before using. Dopamine (98%) was obtained from Alfa Aesar China (Tianjin) Co., Ltd, which was stored under $25^{o}C$. Tris (hydroxymethyl) aminomethane (99%), Methylene blue (MB, 98%) were obtained from Aladdin China (Shanghai) Co., Ltd. Titanium Dioxide ($TiO_2$, Anantase, 5-20 nm) was got from Hangzhou Wan Jingxin Materials Co., Ltd. Butyl titanate ($Ti(OBu)_4$), heptadecafluorononanoic acid (HFA) were received from Sinopharm Chemical Reagent. Hexane, heptane, toluene and tetrachloromethane were obtained from Aladdin China (Shanghai) Co., Ltd. Pump oil and vegetable oil were obtained from the local supermarket. Deionized water was used in the whole process.

**Characterization:** Hitachi-S4800 field-emission scanning electron microscope (FE-SEM) was used to investigate the morphology of the PLA non-woven fabrics before and after modification. The morphology of PLA fiber was also observed by optical microscopy (BX 51TF Instec H601). Water contact angles (WCA) measurements were carried out at room temperature using the sessile drop method and image analysis of the drop profile (OCA-20). The water (Milli-Q) droplet volume was 3.0 μL, and average of three measurements was made to determine the surface wettability. The chemical composition of PLA non-woven fabric before and after modification was analyzed by X-ray photoelectron spectroscopy (XPS, Shimadzu Axis Ultradld spectroscope), using Mg-K (alpha) as radiation resource. X-ray diffraction (XRD) was performed on a Rigaku R-Axis Spider diffractometer with an image plate detector using Cu Kα radiation (λ = 1.5418 Å) and a graphite monochromator. The instrument was controlled by

Rapid/XRD diffractometer control software (version 2.3.8, Rigaku Americas Corp., The Woodlands, TX).

**Preparation of PDA/PLA non-woven fabric:** Briefly, the pristine PLA non-woven fabric was washed thoroughly with deionized water and sonicated for 3 h. Then the PLA non-woven fabric was submerged in a glass tube containing 2 mg/mL dopamine (10 mM, Tris-buffer solution), the reaction mixture was stirred at $55^{o}$C 200 r/min for 12 h.

**Preparation of the advanced PLA non-woven fabric with controllable wettability:** Firstly, different mass proportion (1. 100:1, 2. 100:1.5, 3. 100:2, 4. 100:2.5, 5. 100:3) of $Ti(OBu)_4$ and HFA were mixed (According to the mass ratio about PLA non-woven fabric, $Ti(OBu)_4$ and HFA, it can be estimated the relative amount of fluorine substance is less than 0.378%, indicating above 99.622% ingredients are environmental friendly). Ethanol and deionized water were then added into the mixed solution. The mixture was dispersed by sonication for 10 min. Secondly, the PDA/PLA non-woven fabric and $TiO_2$/ethanol dispersion (50 mL, 0.067 mg/mL) were mixed and sonicated for 2 h to make a homogenous solution. Lastly, different type of the $Ti(OBu)_4$-HFA emulsion (1 mL) was added into the above solution. The reaction mixture was stirred at $60^{o}$C, 210 r/min for 12 h. Each as-prepared PLA non-woven fabric was rigorously rinsed with ethanol to remove the $TiO_2$ particles undecorated.

**Oil/Water Separation:** For oil/water separation, organic solvents and water were dyed by oil red O and $CuSO_4$, respectively. An oil/water mixture consisting of 50 mL organic solvent and 50 mL water were poured directly onto the separation setup and separated through the superhydrophobic and superhydrophibic PLA non-woven fabric, respectively.

The separated liquids were collected with a test tube and a beaker to determinate the separation efficiency.

**Sorption of organic solvents:** Firstly, 2 mg oil red O (an organic dye) was added in 15 mL hexane and the mixture was sonicated for 10 min to form a homogeneous solution. Secondly, hexane was added to water. The hexane droplet was in the upper layer of water due to the different density of hexane and water, which can form a homogeneous oil layer. Lastly, a superhydrophobic PLA non-woven fabric was placed in contact with hexane until the oil was completely absorbed. The sorption of other organic solvents was performed by the same procedure. It is emphasized that the test should be done quickly in order to avoid evaporation of organic solvents, especially for those with low boiling points. The absorption capacity $G$, was calculated according to Equation:

$$G = \frac{m_2 - m_1}{m_1} \text{ (Equation 1)}$$

where $m_1$ and $m_2$ are the weights of the dry and wet superhydrophobic PLA non-woven fabric, respectively. The ratio of water and oil absorbed by the superhydrophobic PLA non-woven fabric was also measured by squeezing it out.

**UV-Degradation Performance:** Firstly, 50 mL methylene blue (MB, 2 mg/L) aqueous solution and the superhydrophilic PLA non-woven fabric were put into a Petri dish. Lastly, this equipment was irradiated by UV-light vertically for a certain time (250 W), and 2 mL solution was taken out for the test of MB absorbance. The degradation rate ($\eta$, %), was defined as:

$$\eta = \frac{A_0 - A_t}{A_0} \text{ (Equation 2)}$$

where $A_0$ is the absorbance in 665 nm wavelength of raw solution, and $A_t$ is the absorbance in 665 nm wavelength of solution at every time. (Note: 665 nm is the characteristic wavelength of MB aqueous solution in visible light.)

**The particle size of TiO$_2$ according to the Scherrer formula:**

$$D = \frac{K\lambda}{\beta \cos\theta} \quad \text{(Equation 3)}$$

where $K$ is the Scherrer constant, $\lambda$ is the wavelength of X-ray, $\beta$ is the diffraction peak, and $\theta$ is the corresponding diffraction angle.

**RESULTS AND DISCUSSION**

**Wetting Behaviors.** The oil/water separation ability is closely dependent on the surface wettability. The surface wettability of PLA non-woven fabric before and after modification was investigated by virtue of water contact angle (WCA) and oil contact angle. As shown in **Figure 2**, the wettability of unmodified PLA non-woven fabric indicates a hydrophobic surface (**Figure S1**), showing simultaneously oleophilicity and hydrophilicity. Upon modification with PDA, PLA non-woven fabric becomes more hydrophilic with a WCA of 23 ± 2.3° (**Figure S2**) due to the introduction of abundant hydroxyl and amino groups on the surface of PLA fiber[29]. However, the PLA non-woven fabric has shown different wettability upon regulating the relative proportion of Ti(OBu)4 and HFA (**Figure 2A**). When the mass proportion is 100:1, the PLA nonwoven fabric holds superhydrophilicity (**Figure 2B**). In the liquid/air/solid three-phase system, a water droplet immediately spreads out and permeates into the fabric and the WCA is nearly 0° (**Figure 2C, Movie S1**). Moreover, it also presents unique under-water superoleophobic characteristic for various organic solvents (**Figure 2F**), which make it a good candidate for

oil/water separation. On the contrary, the PLA non-woven fabric is superhydrophobic (**Figure 2D**)
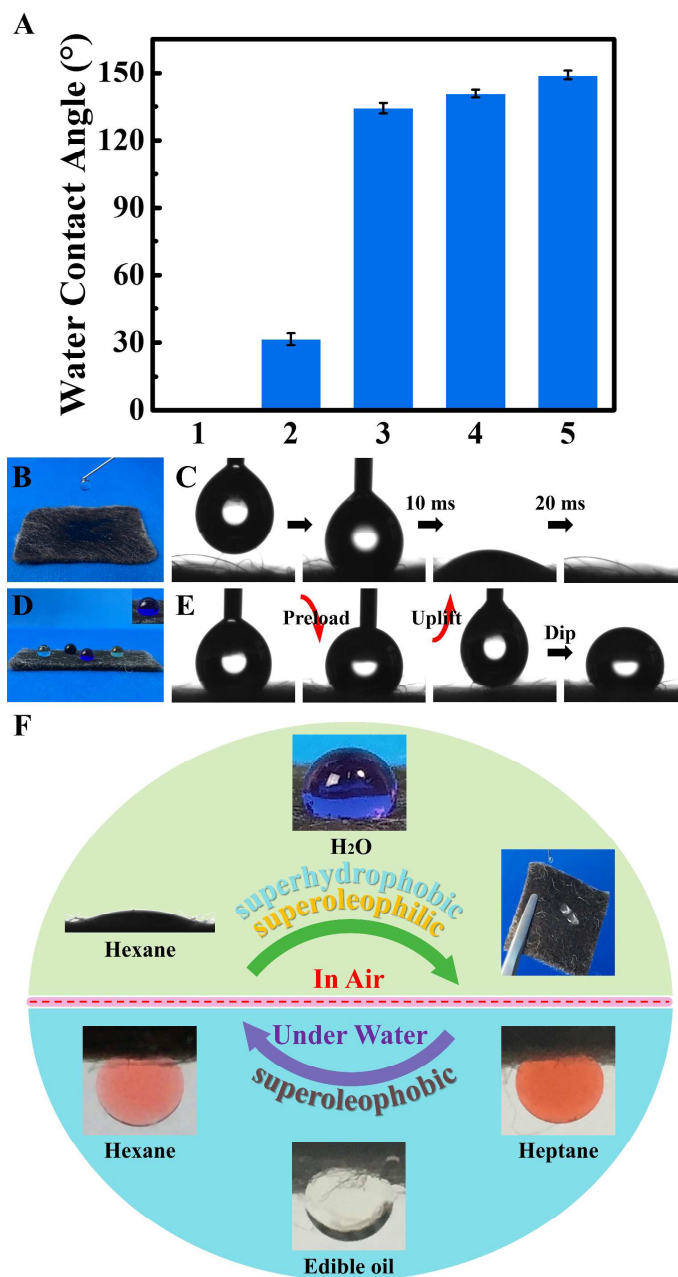


**Figure 2**. (A) The wettability behavior of PLA non-woven fabric according to the relative proportion of $Ti(OBu)_4$ and HFA (1. 100:1, 2. 100:1.5, 3. 100:2, 4. 100:2.5, 5. 100:3). (B) An as-prepared superhydrophilic PLA non-woven fabric with water droplets on the surface. (C) A water droplet makes contact with the superhydrophilic PLA non-woven fabric surface and it immediately spreads out and permeates into the fabric within 2 s. (D) An as-prepared superhydrophobic PLA non-woven fabric with water droplets on the surface (dyed with $CuSO_4$

and FeCl$_3$, respectively). (E) A water droplet is difficult to permeate into the superhydrophobic PLA non-woven fabric. (F) The wettability behavior of the superhydrophobic PLA non-woven fabric in the liquid/air/solid three-phase interface (upper) and the superhydrophilic PLA non-woven fabric underwater with oil on the surface (below).

and a water droplet is difficult to permeate into the fabric (**Figure 2E, Movie S2 and S3**) when the mass proportion of Ti(OBu)$_4$ and HFA is 100:3. Under this condition, a water droplet is difficult to attach on the superhydrophobic PLA non-woven fabric, and it bounces off quickly once in contact with the slightly tilted superhydrophobic PLA non-woven fabric (**Figure 2F**).[37]

The reason why the as-prepared PLA non-woven fabric presented different wettability is that the surface wettability is governed by surface chemistry and morphology[38-39]. Chemical composition determines the surface free energy, and a lower surface energy leads to higher hydrophobicity. In addition, the surface roughness is very important to surface hydrophilicity because of the 2D or 3D capillary effect, that is, roughness will amplify the wetting behavior of substrates. All these results confirmed that materials with different wettability can be realized by simply controlling the relation ratio of the same substance, which is convenient to construct special wettability materials for oil/water separation.

**Surface morphology.** Furthermore, the microstructures of the as-prepared superhydrophilic and superhydrophobic PLA non-woven fabric were characterized by scanning electronic microscopy (SEM). As shown in **Figure S3 and S4**, the PLA non-woven fabric displays three-dimensional porous network structures consisting of smooth microfibers (20-25 μm). Upon being attached by TiO$_2$ particles (5-20 nm) and HFA, a number of granules randomly distribute on the surface of PLA fibers, and the fabric structure remains unchanged. High-resolution SEM images indicated that the TiO$_2$ nanoparticles overlap densely and form poly-dispersive aggregates even deeply imbed inside the non-woven fabric attributed to the high aperture size of the PLA non-woven fabric (**Figure 3A, 3B**). The difference between the superhydrophilic and superhydrophobic PLA

non-woven fabric is that $TiO_2$ granules is uniformly distributed upon the surface of the superhydrophilic PLA non-woven fabric (**Figure 3A**), whereas accumulated seriously in the superhydrophobic PLA non-woven fabric (**Figure 3B**). In addition, the optical microscopy images also clearly show the macroscopic rough surfaces of PLA fibers (**Figure S4**). The particulate morphology endows hierarchical rough structures to the PLA non-woven fabric, which is essential to build robust super-wetting materials.

**Chemical Composition.** The chemical composition of the hierarchical PLA non-woven fabric was further analysed by X-ray photoelectron spectroscopy (XPS). For the pristine PLA non-woven fabric, only peaks of C and O are detected and no other impurities can be observed (**Figure S5**). In the XPS pattern of superhydrophilic PLA non-woven fabric, typical N 1s, Ti 2p, F 1s peaks appear at around 399 eV, 456 eV and 608eV, mainly assigning to the PDA, $TiO_2$ and HFA, respectively (**Figure 3C, S6B and S7A**). These results also appear in the XPS of superhydrophobic PLA non-woven fabric (**Figure 3D, 3F, S6C and S7B**). From the XPS elemental spectra, C, O, N, Ti, F, are distributed on the PLA non-woven fabric surfaces, which suggest that $TiO_2$ particles and HFA are coated on the PLA non-woven fabric. Furthermore, the Ti 2p spectrum of superhydrophilic PLA non-woven fabric has a remarkable difference with that of superhydrophobic PLA non-woven fabric (**Figure S7**), which is in good agreement with the stoichiometric ratio of the corresponding F element in these fabrics. The X-ray diffraction (XRD) pattern of the superhydrophilic PLA non-woven fabric (**Figure 3E**) exhibits the characteristic diffraction peaks at around $18.64^o$, $25.34^o$, $37.82^o$ corresponding to the (002), (101), (004) reflections of anatase $TiO_2$ respectively. In addition, according to Scherrer formula[40], the particle size of $TiO_2$ (101) is about 8.3 nm (**Figure S8**) and $TiO_2$ (002) is about 13.0 nm

(**Figure S9**), which endows the superhydrophilic PLA non-woven fabric with photo-

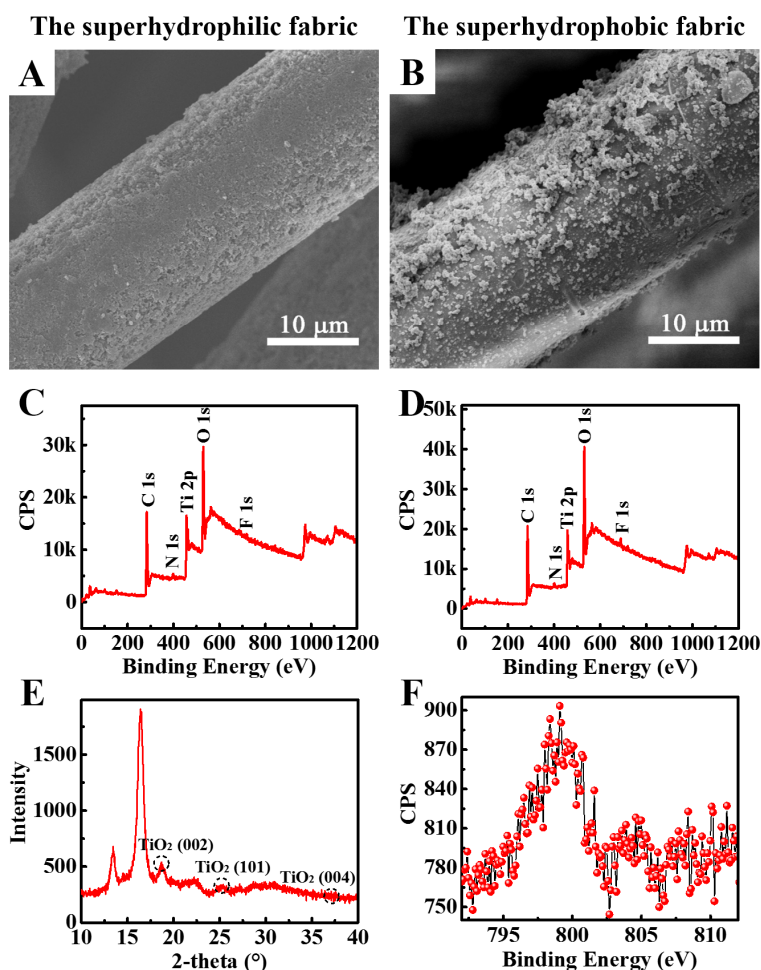catalysis degradation of organic pollutants in water.



**Figure 3.** The SEM images of the superhydrophilic PLA non-woven fabric (A) and superhydrophobic PLA non-woven fabric (B). The XPS spectrum (C) and XRD spectrum (E) of the superhydrophilic PLA non-woven fabric. (D) The XPS spectrum of superhydrophobic PLA non-woven fabric and F 1s (F).

**Separation Performance.** The super-wettability makes the advanced PLA non-woven

fabric a promising candidate for oil/water separation. The controllable wettability

between superhydrophobicity and supehydrophilicity allow us to utilize PLA non-woven

fabric to switch selective oil/water separation. The practical oil/water separation was carried out in a simple suction filtration setup, as shown in **Figure 4**. A certain volume of n-hexane (dyed with oil red O) and water (dyed with $CuSO_4$) is poured into the separation setup, the water quickly penetrates into the superhydrophilic PLA non-woven fabric and the oil is collected on the surface (**Figure 4A**). No oil in the collected water can be seen, showing a very high separation efficiency of the superhydrophilic PLA non-woven fabric. Whereas, as to the superhydrophobic PLA non-woven fabric, the oil penetrates quickly while the water is collected on the surface (**Figure 4B**). These results indicated both the superhydrophilic and superhydrophobic PLA non-woven fabrics hold excellent performance for the treatment of wastewater. This is a significant improvement for the original PLA non-woven fabric, which cannot use in oil/water separation (**Movie S4**). The reliability of the superhydrophobic or superhydrophilic PLA non-woven fabric was also tested by carrying out cyclic experiments for oil/water separation, which is an important criterion for practical applications. After each experiment, the fabric maintains the high flux even after 10 recycle numbers, which indicates good cyclic performance of the advanced PLA non-woven fabric (**Figure 4C and 4D**). Besides, there is almost not any change on the surface morphology of PLA fiber (**Figure S10**) after cyclic separation. Hence, it is considered that the separation does not destroy the surface rough structures and composites of the non-woven fabric coated with PDA and micro/nano particles, which lead to the robust surface wettability and stable separation performances.

**Oil-Absorption Performance.** With porous structure and flexibility, the superhydrophobic PLA non-woven fabric exhibits a high performance for adsorption of oils and organic solvents from industrial wastewater. As shown in **Figure 5A**, n-hexane

floating on water can be absorbed quickly by the superhydrophobic PLA non-woven fabric within 3 s. Similarly, high-density tetrachloromethane could be rapidly absorbed within 3 s (**Figure 5B**). Significantly, water is hardly absorbed during the oil-absorption process, indicating the excellent selective separation capacity of the superhydrophobic PLA non-woven fabric. To further investigate the absorption capacity, the oil-absorption rate $G$ is employed to evaluate quantitatively oil-absorption capacity. Various organic solvents and oils were selected as common model pollutants. It is indicated that the superhydrophobic PLA non-woven fabric has a very high oil-absorption capacity (**Figure 5C**).



**A    The superhydrophilic PLA non-woven fabric**
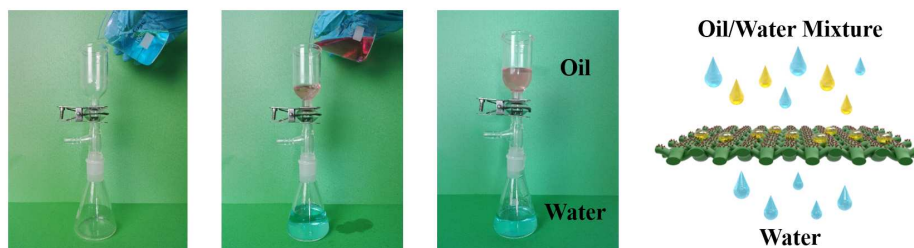
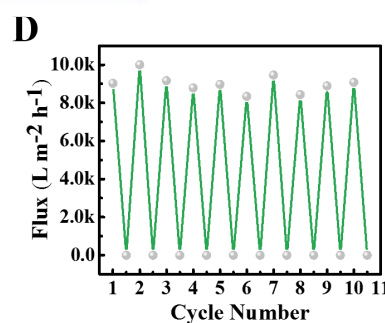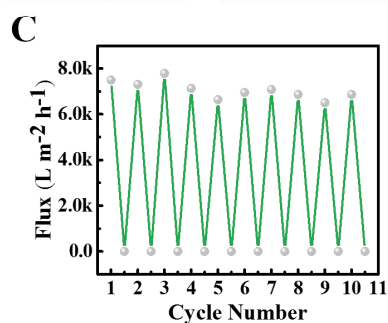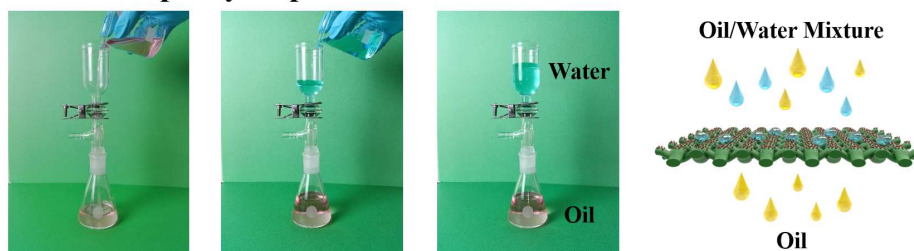**B    The superhydrophobic PLA non-woven fabric**

**Figure 4.** (A, C) Photograph of n-hexane/water separation and the recycled separation fluxes of hexane/water mixture using the supehydrophilic PLA non-woven fabric, the water quickly penetrates through and the oil is collected on the surface. (B, D) Photograph of n-hexane/water separation and the recycled separation fluxes of hexane/water mixture using the superhydrophobic PLA non-woven fabric, the oil quickly penetrates through and the water is collected on the surface.
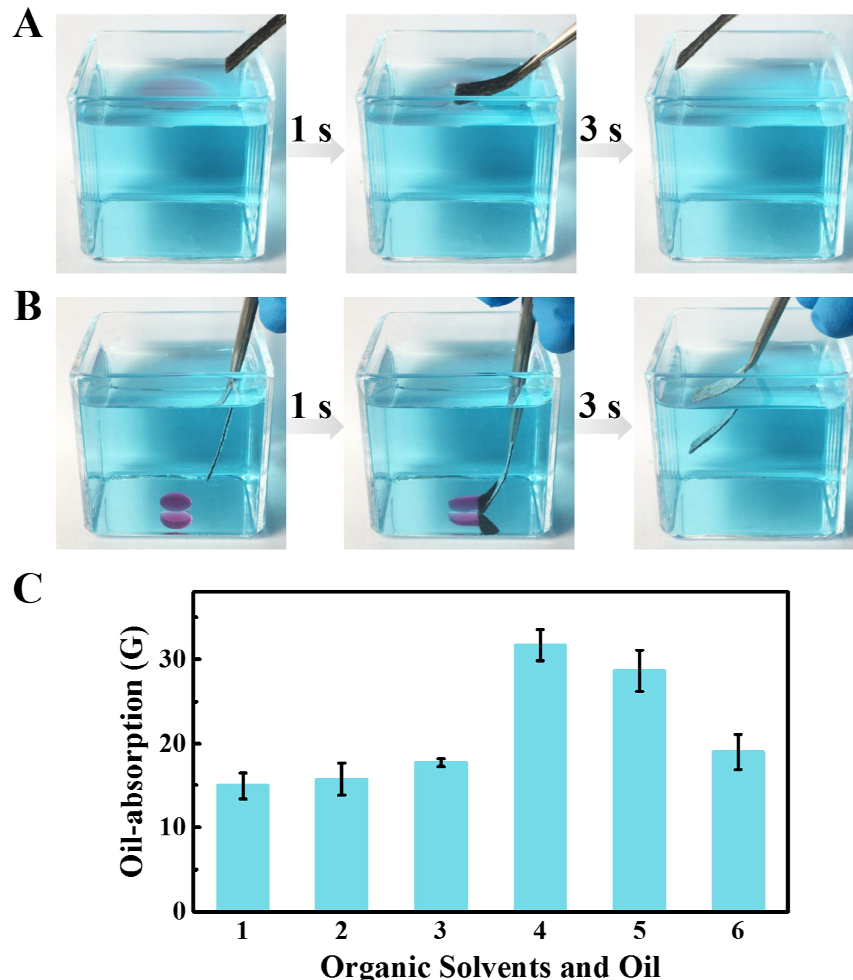




**Figure 5.** Photographs of the removal of n-hexane (A) and (B) tetra chloromethane by the superhydrophobic PLA non-woven fabric. (C) Absorption capacity of the superhydrophobic PLA non-woven fabric for various organic liquids (1. hexane, 2. heptane, 3. toluene, 4. tetrachloromethane, 5. pump oil, 6. vegetable oil).

**UV-Degradation Performance.** Catalytic degradation is a practicable means to remove water-soluble organic contaminants[33]. Integrating appropriate catalysts with underwater superoleophobic separation materials not only can separate oil from water but also decompose the organic contaminants in water. It is generally known that titanium dioxide

($TiO_2$) is a well-known photocatalytic material that can generate plenty of reactive species, including hydroxyl radicals and superoxide anions, under UV irradiation[41-42]. In this work, the catalysis capability of this supehydrophilic PLA non-woven fabric was investigated by immersing the membrane into MB aqueous solution. As shown in **Figure 6**, with increasing time of UV irradiation, a gradually declining intensity of the characteristic peaks of MB aqueous can be observed (**Figure 6A**). The degradation rate ($\eta$, %) is employed to evaluate the capacity of degradation. After the same irradiation condition, the $\eta$ of the blank sample, PDA/PLA and the superhydrophilic PLA non-woven fabrics are degraded 41.4%, 66.0%, 86.9%, respectively (**Figure 6B**), showing a superior degradation effect of the superhydrophilic PLA non-woven fabric. In addition, the degradation process of the superhydrophilic PLA non-woven fabric can be recycled stably. After each cycle, the degradation rate changes within 3-7%, and the microstructure and component of the superhydrophilic PLA non-woven fabric are hardly affected (**Figure 6C**), indicating the excellent reusability of the superhydrophilic PLA non-woven fabric and stable modification of $TiO_2$ nanoparticles. There are two main factors for the degradation performance of the superhydrophilic PLA non-woven fabric. One is attributed to the special wettability of the superhydrophilic PLA non-woven fabric, which has enlarged the effective contact area with the water-soluble organic matters. Another is due to the photo-degradation property of $TiO_2$ nanoparticles (**Figure 6D**). After UV irradiation, reactive oxygen species with strong redox activity are generated due to the electron excitation and transition. These as-formed reactive oxygen species can degrade organic compounds into $H_2O$, $CO_2$ and other small molecule compounds[43-44]. This self-cleaning behavior of the superhydrophilic PLA non-woven fabric may be of great

significance for practical application by reducing the use of solvent and decreasing the
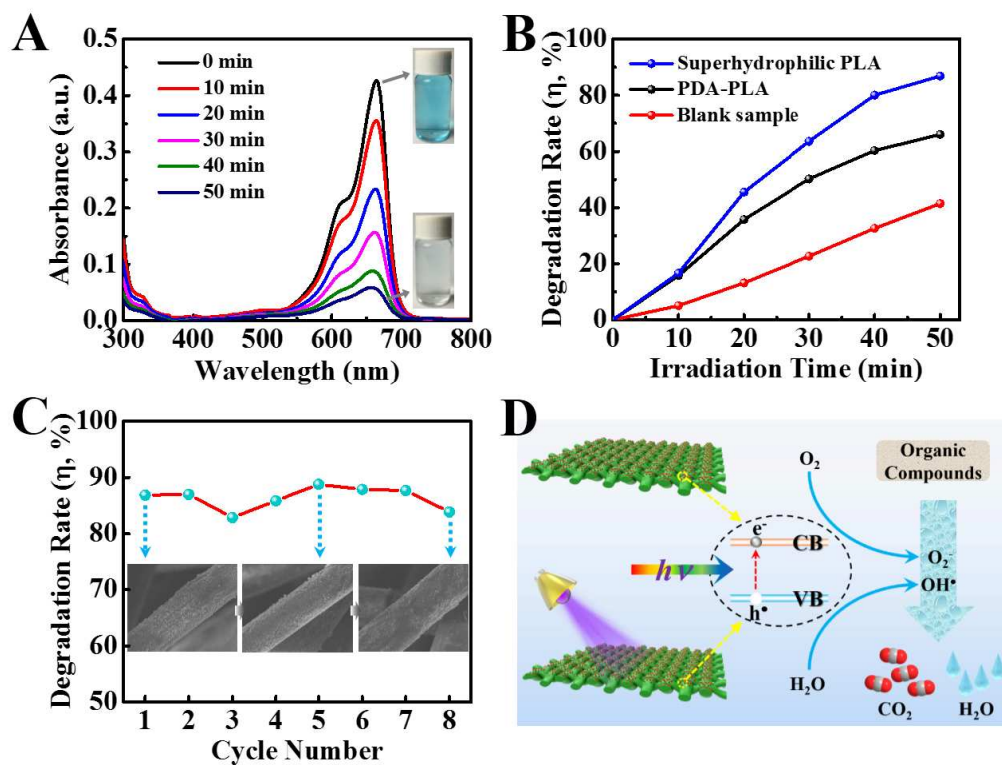
cost of recycling.



**Figure 6.** (A) The superhydrophilic PLA non-woven fabric was applied to degrade MB solution via UV-light. The absorbance of MB solution with increasing time of UV irradiation. (B) The degradation rate of MB solution via different samples. (C) The degradation rate of the MB solution using the superhydrophilic PLA non-woven fabric versus the recycle numbers of degradation process. Insert: SEM of the superhydrophilic PLA non-woven fabric before and after several degradation processes. (D) Illustration of the photocatalytic mechanism of the prepared superhydrophilic PLA non-woven fabric.

**CONCLUSION**

In summary, we have developed a convenient strategy to fabricate cost-effective super-wetting

PLA non-woven fabrics for the effective separation of oil/water mixtures. Interestingly, the

wettability of such fabrics can be regulated by adjusting the relative proportion of chemical

component. The resulting super-wetting PLA non-woven fabrics exhibit high absorption capacity

and high selectivity when they are employed as absorptive materials and oil/water separation materials. In addition, the superhydrophilic PLA non-woven fabric possesses excellent photo-catalysis degradation ability for variety of soluble organic pollutants property under UV irradiation, which is significant in saving solvents and recycling materials. With high absorption capacity and selectivity, photo-degradation property, biodegradability, these advanced PLA non-woven fabrics may provide solutions to complex oily water treatment.

## Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1039/c000000x/.

Static WCA measurements for PDA@PLA non-woven fabrics; SEM images and optical images of the original PLA non-woven fabric, modified PLA non-woven fabric; XPS spectrum of the raw PLA non-woven fabric; the Ti 2p XPS spectrum of superhydrophilic PLA non-woven fabric and superhydrophobic PLA non-woven fabric; movies of the wettability of the modified PLA non-woven fabric; movie of the separation performance of the original PLA non-woven fabric.

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## NOTES

The authors declare no competing financial interest.

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TOC Entry: A facile strategy to realize the controllable wettability on polylactic acid (PLA) non-woven fabric has been developed for efficient water purification.