



Contents lists available at ScienceDirect

Arabian Journal of Chemistry

journal homepage: www.ksu.edu.sa

Review article

Superwetting functional polyurethane as a promising porous material for oily water treatment

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ARTICLE INFO

Keywords:

Oil-water separation
Polyurethane
Porous material
Superhydrophobicity

ABSTRACT

Oil spills and industrial oily wastewater during petroleum and chemical production and transportation have caused serious damage to water resources and the environment. Therefore, it is of great significance to develop new materials and new methods for oil pollution control. Recently, polyurethane (PU) polymers have been proven to be promising candidates for the fabrication of superhydrophobic and superoleophilic materials for oil-water separation due to their low cost, strong absorptive capacity, good elasticity, and ease of large-scale manufacturing. In this review, we summarize the recent advances of superhydrophobic PU-based materials for oil-water separation. The synthesis methods of porous PU based two-dimensional (2D) membrane and three-dimensional (3D) foam are introduced. Furthermore, the strategies of modifying the PU-based foam to enhance its superhydrophobicity through the synergistic effect of increasing surface roughness and reducing surface energy are highlighted, which greatly promotes its application in oil-water separation. Finally, the common methods for the recycling of oil-absorbing materials are discussed. This work has important reference significance for PU-based materials in solving oil pollution.

1. Introduction

Water pollution is one of the most significant environmental and natural resource issues of the 21st century. Oil spills are an important cause of serious pollution in surrounding waters (Huynh et al., 2021, Rojas and Horcajada, 2020, Schrope, 2010). For instance, Gulf of Mexico oil spill in 2010 resulted in an estimated 200 million gallons of oil spilled (Camilli et al., 2010, Ryerson et al., 2012). Despite several years of effort

by British Petroleum, only partial cleanup has been achieved, and comprehensive oil pollution cleanup is still incomplete. Water bodies polluted by oil often contain toxic chemicals, causing the death of marine life and severe damage to underwater vegetation habitats, seriously threatening the health of coastal residents, and even causing catastrophic effects on the ecosystem (Ivshina et al., 2015, Qu et al., 2022, Widger et al., 2011). Therefore, controlling oil pollution in water bodies is of great significance and has become a current hot research field.

Abbreviations: 2D, two-dimensional; 3D, three-dimensional; APT, attapulgit; cMWNTs, carboxyl multi-walled carbon nanotubes; CNTs, carbon nanotubes; DDT, *n*-dodecyl mercaptan; FAS, heptadecafluoro-1,1,2,2-tetrahydrodecyltrimethoxysilane; FD-silica, fluorinated silica; FMA, 1H,1H,2H,2H-heptadecafluorodecyl methacrylate; F-OV-POSS, fluorated octavinyl polyhedral oligomeric silsesquioxane; FPU/FeOOH, flexible PU modified with FeOOH; GO, graphene oxide; g-C₃N₄, graphitic-carbon nitride; HDPE, high-density polyethylene; HFA, heptadecafluorononanoic acid; IP, interfacial polymerization; MMA, methylmethacrylate; MWCNT, multi-walled carbon nanotube; NIPS, nonsolvent-induced phase separation; NPs, nanoparticles; OAP, o-aminophenol; OCA, oil contact angle; OTEOS, octyltriethoxysilane; OTS, octadecyltrichlorosilane; PA, palmitic acid; PANI, polyaniline; PDMS, polydimethylsiloxane; PE, polyethylene; PEI, polyethyleneimine; PFOA, perfluorooctanoic acid; PNIPAM, poly(*n*-isopropylacrylamide); PP, polypropylene; PPy, polypyrrole; PS, polystyrene; PT, polythiophene; PU, polyurethane; PVC, polyvinyl chloride; RGO, reduced graphene oxide; SA, stearic acid; SiMA, 3-[tris[(trimethylsilyloxy)silyl]propyl]methacrylate; SiPUF, silicone polyurethane-coated fabric; TEOS, tetraethoxysilane; TIPS, thermally induced phase separation; TMC, 1,3,5-benzenetricarbonyl trichloride; TMHFDS, trimethoxy(1H,1H,2H,2H-hepta-decafluorodecyl) silane; TPU, thermoplastic polyurethane; VTEOS, vinyltriethoxysilane; WCA, water contact angle.

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Received 13 September 2023; Accepted 30 March 2024

Available online 4 April 2024

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So far, a variety of oil pollution treatment methods have been proposed. They can be roughly divided into (i) physical methods (Liu et al., 2021), such as extraction, centrifugation, suction etc.; (ii) chemical methods, including the use of dispersants, surfactant degradation, and in-situ combustion (Aurell and Gullett, 2010, Kujawinski et al., 2011); (iii) biological methods (Davoodi et al., 2020, Okeke et al., 2022), such as landfill and microbial decomposition; and mechanical treatment (Etkin and Nedwed, 2021). However, these conventional methods generally suffer from limitations such as high costs, high energy consumption, production of toxic compounds during usage, low efficiency in oil–water separation, poor material recyclability, and potential secondary environmental pollution. Therefore, the development of new materials that are efficient, environmentally friendly, recyclable, selectively absorbent has become a top priority.

Initially, researchers explored natural materials with porous structures and high surface areas to adsorb oil, but these materials generally exhibit limited adsorption capacity and reusability (Gao et al., 2023, Ge et al., 2018, Li et al., 2023b, Su et al., 2022). With advances in synthetic materials, the focus has turned to chemically synthesized high-capacity oil-absorbing materials. In recent years, various novel oil-absorbing

materials with high absorption capacities and stable cyclic performance have attracted widespread attention. (Han et al., 2022; Jia et al., 2023, 2022; Gupta et al., 2017, Jiang et al., 2022). Among these, 3D porous materials such as PU foams and aerogels are considered ideal due to their ultra-high porosity (>95%) and excellent flexibility (Baig et al., 2021, Chu et al., 2015, Ma et al., 2016, Peng et al., 2019, Wang et al., 2015, Zuo et al., 2020). PU foam stands out for its low cost, good stability, high porosity, high permeability, and potential for recycling waste PU plastics, making it a strong candidate for large-scale industrial production of oil-absorbing materials.

However, due to the intrinsic properties of PU foams, their poor hydrophobicity hinders their selective separation of oil–water mixtures. Therefore, the modification of PU foam with suitable functional agents and materials has become an important field of current research (Bhagwat and Jaspal, 2023, Hailan et al., 2021, Pinto et al., 2018). Inspired by superwetting phenomena in nature, researchers have developed many superhydrophobic and superoleophilic porous PU materials (Abu-Thabit et al., 2022, Guan et al., 2019, Yong et al., 2019). These materials can directly absorb oil from water without causing secondary pollution. And the adsorption materials can be reused, which

Table 1
Comparison of different modified PU materials.

Types	WCA/OCA(°)	Repetition times	Separation efficiency/adsorption capacity	References
TPU@g-C ₃ N ₄ @PFOA	WCA 18.9 OCA 151	–	99.9 %	Mir et al., 2022
SiPuF	WCA 150	50	99 %	Mao et al., 2023a
SiO ₂ /PU	WCA 152.7–154.9	30	98.5 %	Gu et al., 2020a
poly(SiMA-co-MMA)	WCA 178	–	–	Hwang et al., 2011
APT/PU	WCA 152	50	99.87 %	Li et al., 2016b
TiO ₂ /PU	OCA 150	40	99 %	Li et al., 2016c
ZnO/PU	WCA 150 OCA 150 (switchable)	–	99 %	Yan et al., 2016
SiO ₂ /TPU	WCA 139.2	–	–	Wang et al., 2011
PU-C ₆ F ₁₇	WCA 150	100	99.3 %	Fang et al., 2016
TPU-PNIPAM	WCA 150.2	–	99.26 %	Ou et al., 2016
GPUF	WCA 151 OCA 0	150	90–316 g•g ⁻¹	Anju and Renuka, 2020
MWCNTs@PU	WCA 157.4 ± 1.1	10	–	Chen et al., 2020
CNTs/PDMS-coated PU	WCA 140 ± 3	–	99.97 %	Wang and Lin, 2013
HFA-TiO ₂ /PU	OCA 153	–	–	Xu et al., 2015
TPU/cMWNTs	WCA 132 ± 1.6	10	14.21–24.07 g•g ⁻¹	Juraj et al., 2022.
TPU/cMWNTs	WCA 151 OCA 0	40	98.4 % 6.9–42.3 g•g ⁻¹	Ye, et al., 2020
Fe ₃ O ₄ /PU	WCA 153.7 ± 2.7	10	35 g•g ⁻¹	Liu et al., 2015
Ni-Co/PU	WCA 157	150	–	Yang et al., 2023
Fe ₃ O ₄ /PU	WCA 154.7	–	4–6.3 g•g ⁻¹	Li et al., 2018
OTS/PU	WCA 156 OCA 0	5	92.6 % 20–25 g•g ⁻¹	Liang et al., 2019
HDPE/PU	WCA 150	10	32–90 g•g ⁻¹	Cheng et al., 2018
PPy-PA/PU	WCA 140	10	22–62 g•g ⁻¹	Khosravi and Azizian, 2015
PDA/PPy/PANI/PU	WCA 164	20	99 % 44 g•g ⁻¹	Satria and Saleh, 2023
PANI/PU	WCA 150 OCA 0	20	44–95 g•g ⁻¹	Li et al., 2020b
PU-IP-PA sponge (TMPTA/EHA)/PU	WCA 161	500	16.5–29.9 g•g ⁻¹	Zhang et al., 2016
TMNC/PU	WCA 150	6	93.6 %	Han et al., 2011
PU@ZnO@Fe ₃ O ₄ @SA	WCA 161	100	99 % 32–108.9 g•g ⁻¹	Wang et al., 2013 Tran and Lee, 2017
FPU/FeOOH	WCA 146.4	50	44 g•g ⁻¹	Zhou et al., 2022.
RGO/OAP/PU	WCA 179	10	24.19–80.28 g•g ⁻¹	Jamsaz and Goharshadi, 2020
3D TPU	WCA 143	40	99.5 % 5.95–40.60 g•g ⁻¹	Qin et al., 2019
TiO ₂ -copper foams	WCA 160	50	99 %	Zhou et al., 2018
TPU/Fe ₃ O ₄ @FAS	WCA 153	50	99.1 % 6.0–41.1 g•g ⁻¹	Shi et al., 2021
PU/diatomite	WCA under water 153 ± 3 OCA under oil 152 ± 2	10	99 %	Wu et al., 2022
F-OV-POSS/PU	WCA 155.8 OCA 0	20	99 %	Chen et al., 2019b
SiPUF	WCA 150	60	99.3 %	Mao et al., 2023a

overcomes many shortcomings of traditional methods. In addition, these materials can selectively adsorb oil components from water without changing the properties of the oil, allowing the recovered oil to be recycled. Currently, the research and development of PU modification is progressing rapidly, and functional porous PU is proven to be a promising candidate for fabricating superhydrophobic and superoleophilic materials for oil–water separation. From this perspective, we review the main progress of hydrophobic/lipophilic functional PU (Table 1) in oily water treatment in the following three aspects: preparation method, modification strategy and recycling method.

2. Physicochemical properties of oil–water mixtures

The purification of oily water is one of the important issues of environmental protection. The primary factor that needed to be considered in the oil–water separation is the physicochemical properties of oil–water mixtures. Traditional techniques, such as centrifuges, flotation, coalescers and oil skimmers, can be used to some extent to separate oil–water free mixture types of oil–water emulsions. But it cannot be used to achieve emulsified oil–water separation (Si and Guo, 2015). Thus, superwetting materials with widely different affinities toward oils and water are highly desirable and open a new door for oil–water separation technology. In fact, after years of research, the separation method of oil-free water mixture has become relatively mature.

For the complex oil–water emulsions, their separation is much challenging because the diameter of the dispersed phase is too small. One type is water-in-oil (W/O) emulsion, in which oil is the continuous phase. The oil and water separation can be achieved by using a superhydrophobic/superoleophilic materials with appropriate pore size. Another type is oil-in-water (O/W) emulsion, in which the oil is the dispersed phase in the form of small droplets distributed in water. It needs to be demulsified first so that the material comes into contact with the oil droplets for separation.

In addition, the physicochemical properties of oil, such as oil viscosity, polarity, surface tension, etc. also significantly affect the performance of oil–water separation (Li et al., 2023a). Typically, the higher the viscosity of the oil, the oil absorption and separation efficiency decreases. The higher the viscosity of the oil–water emulsion, the higher the stability of the emulsion and the greater the difficulty of separation. The influence of polarity and surface tension is similar to that of viscosity. The higher it is, the lower the efficiency of oil–water separation.

3. Preparation of PU based oil–water separation material

PU is a synthetic polymer material with wear resistance, tear resistance, bending resistance and excellent mechanical properties (Tai et al., 2021). The primary repeating unit in PU polymers is the urethane group, which is formed through the reaction of polyols with isocyanates. In the preparation of PU, the isocyanate molecules used should contain at least two or more isocyanate groups ($R-(NCO)_n$, $n \geq 2$), and the polyols should contain at least two or more hydroxyl groups ($R'-(OH)_n$, $n \geq 2$) (Gunatillake et al., 2019). The properties of PU depend on the types of polyols and isocyanates used in their synthesis. Flexible long-chain polyols produce soft and elastic polymers, while higher degrees of crosslinking produce rigid and tough polymers. Long chains, low crosslinks produce stretchable polymers, while short chains, high crosslinks produce stiff polymers (Korley et al., 2006, Saralegi et al., 2013). Among them, polymers with average long-chain crosslinks are suitable for producing foams. Due to the presence of crosslinks in PU, an infinite molecular weight and a 3D network structure are formed, thereby preventing PU from softening, and melting when heated (Nik Pauzi et al., 2014).

Currently, PU materials have achieved significant success in the field of oil–water separation. Based on their methods and mechanisms of oil–water separation, PU materials can be divided into two main

categories: 2D PU membranes for filtration and 3D porous PU materials for absorption (Ma et al., 2016, Sultan, 2017).

3.1. 2D PU membranes

Membrane separation technology has attracted more and more attention for the treatment of oily water pollution in recent years (Mir et al., 2022, Sutrisna et al., 2022, Zhu et al., 2014). Among them, superhydrophobic PU membrane with porous structure possesses an excellent mechanical strength, which only allow oil to permeate for effectively selective separation of oil–water mixtures. Generally, these hydrophobic membranes can be prepared by synthesizing a hydrophobic spinning solution, mixing a hydrophobic agent with the spinning solution, or chemically modifying the membrane's surface. The main methods for preparing PU membranes are spray coating, electrospinning, and centrifugal spinning.

3.1.1. Spray-coating method

The spray coating method is characterized by simple process, easy mass production and applicable to various substrates (Feng et al., 2004, Hwang et al., 2011, Richardson et al., 2015, Tu et al., 2007). As shown in Fig. 1A, it involves the spraying of target solution onto a chosen substrate, which is one of the most used membrane preparation techniques (Mao et al., 2023a). Many studies have shown that PU membranes prepared through the spray coating method can be used for oil–water separation (Li et al., 2016a, 2016b). For instance, Li et al. (Li et al., 2016c) sprayed a mixture of TiO₂ nanoparticles (NPs) and PU onto a stainless steel mesh to create a membrane for oil–water separation. The results indicated that only water could permeate through the mesh, while oil was blocked on the mesh, which shows 99.0 % water–oil separation efficiency. The waterborne PU enhanced the cohesion between TiO₂ NPs and the mesh, thereby improving the cyclic stability of oil–water separation. Yan et al. (2016) sprayed a mixture of hydrophobic ZnO NPs and waterborne PU onto a stainless steel mesh for oil–water separation. Interestingly, the mode of oil–water separation can be alternated between the oil-removing to the water-removing, which was realized to the reversible wettability change between the superhydrophobicity and the superhydrophilicity/underwater superoleophobicity by UV irradiation and heat treatment alternately.

3.1.2. Electrospinning method

Electrospinning is one of the most used methods for preparing nanofiber membranes (Greiner and Wendorff, 2007, Huang et al., 2011, Wu et al., 2013). It involves stretching polymer solutions into nanoscale fibers using a high-voltage electric field (Bhardwaj and Kundu, 2010, Kidoaki et al., 2005, Li and Xia, 2004, Liang et al., 2007, Scaffaro et al., 2017). As shown in Fig. 1B, the membranes produced through this method possess good elasticity and mechanical properties, making these PU membranes highly valuable for oil–water separation (Gu et al., 2020b). Wang et al. (Wang et al., 2011) successfully developed a simple method to prepare bead-on-string thermoplastic polyurethane (TPU) membranes using electrospinning technology. After impregnation with a nano SiO₂ solution, the TPU membrane exhibited hydrophobicity with water contact angle (WCA) of 139.2°, suitable for continuous separation of oil–water mixtures. Fang et al. (Fang et al., 2016) used electrospinning to create a self-healing N-substituted PU membrane that retained excellent oil–water separation performance even after chemical or physical damage. Even after 20 cycles of damage and repair, the membrane's oil–water separation efficiency remained above 98 %, laying the foundation for the development of robust oil–water separation advanced materials for oil–water separation.

3.1.3. Centrifugal spinning method

Centrifugal spinning is primarily employed for spinning glass fibers, phenolic resins, and general-grade asphalt carbon fibers, and has been applied to prepare nanofiber membranes in recent years (Atci et al.,

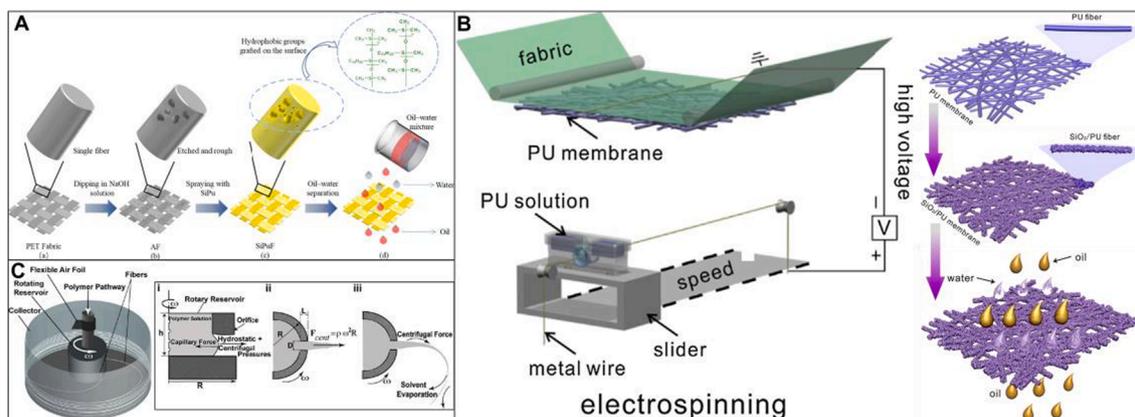


Fig. 1. Schematic diagram of the preparation methods of PU membranes: (A) spray coating, (B) electrospinning, and (C) centrifugal spinning. Adapted and modified from Mao et al. (2023a), Gu et al. (2020b), and Badrossamay et al. (2010).

2022, Xu et al., 2023, Zhang and Lu, 2014). A graphical interpretation of centrifugal spinning of polymer nanofibers is shown in Fig.1C (Badrossamay et al., 2010). An electrical rotor is coupled to a driveshaft where a spinneret is installed. Fibers are spun by forcing the substance into a spinneret's precision nozzles via circular motion. The principle involves using the centrifugal and shear forces generated by high-speed rotation to stretch polymers into fibers. Ou et al. (2016) reported the use of centrifugal spinning to prepare a water gel-coated microfiber composite membrane using PU and poly(N-isopropylacrylamide) (PNIPAM) as raw materials. This composite membrane achieved switchable transitions between superhydrophobicity and superhydrophilicity by altering the temperature, with an oil-water separation efficiency as high as 99.26 %.

3.2. 3D PU foam

Currently, researchers have developed various methods for preparing porous materials using PU as the raw material. As shown in Fig. 2, three well-established techniques including solvent casting, phase

separation, and gas foaming have been widely used for the fabrication of porous PU materials (Janik and Marzec, 2015). In recent years, advanced techniques like 3D printing have also been used to prepare 3D PU foam (Fei et al., 2023, Mauriello et al., 2023). We describe them in detail below.

3.2.1. Solvent casting/particulate leaching

The solvent casting/salting-out method offers the advantages of simple operation and not requiring specialized equipment (Laschke et al., 2010, Ye et al., 2018, Zhang et al., 2022b). In this method, particles of a certain diameter are added as pore-forming agents to a polymer solution of a certain concentration. Then the foam is obtained through solidification, and the particles are subsequently removed via particulate-leaching. Zhu et al. (Zhu et al., 2013) achieved an average pore size of 500 μm and a porosity of up to 93 % in porous PU materials prepared by the solvent-casting and particulate-leaching techniques. However, the morphology of materials produced by this method is greatly dependent on the diameter of the particles used, and selecting

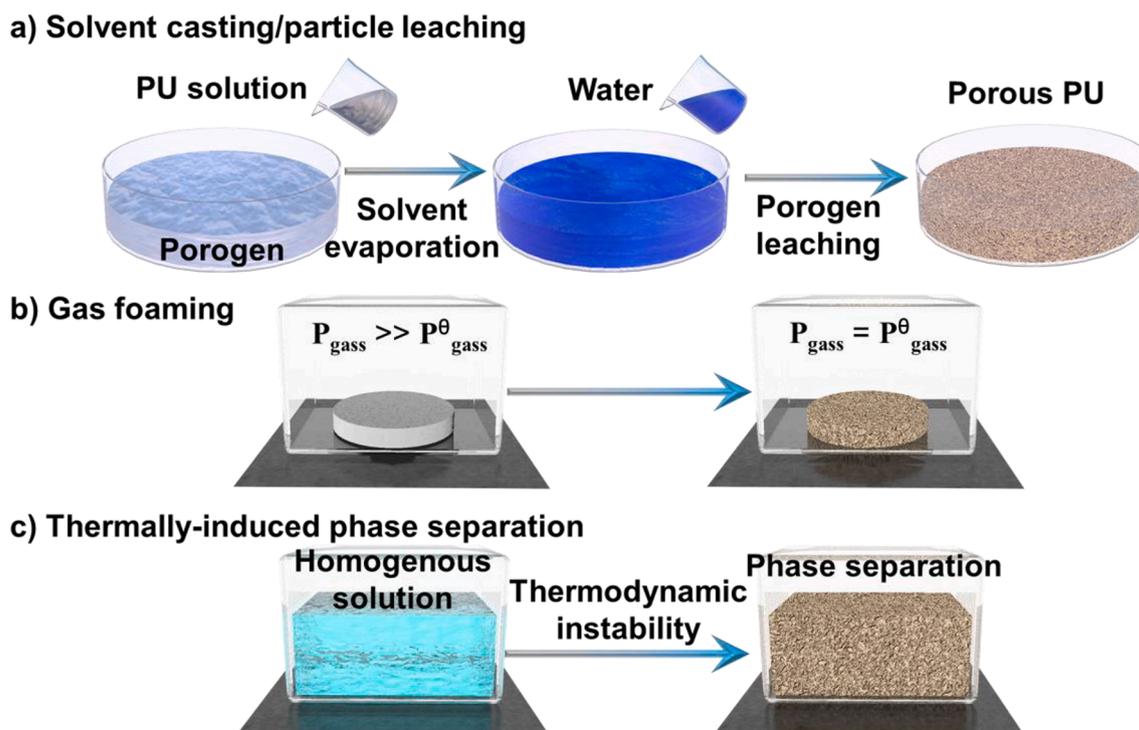


Fig. 2. Schematic diagram of 3D PU foam preparation methods.

suitable particle size is a key factor in the preparation process. In addition, the particles tend to be unevenly distributed in polymer solutions, resulting in non-uniform interconnectivity of pores.

3.2.2. Phase separation

The phase separation method for preparing 3D foams is divided into thermally induced phase separation (TIPS) and nonsolvent-induced phase separation (NIPS). NIPS takes advantage of differences in the solubility of polymers at different temperatures. A homogeneous solution is first obtained at high temperatures, followed by inducing phase separation at low temperatures. The separation solvent is then extracted, and the extractant is removed from the system through evaporation or freeze-drying to produce porous materials (Matsuyama et al., 1999). Phase separation temperature is one of the main factors affecting the properties of porous materials. Guan et al. (2005) performed controlled experiments on PU preparation at the same concentration, it was found that lower temperature resulted in smaller pore sizes.

NIPS can be further categorized into solvent evaporation, vapor-induced precipitation, and immersion precipitation methods. Solvent evaporation method utilizes the difference in solubility of polymers in various solvents. It dissolves the polymer in a mixture of a highly volatile solvent with high solubility and a less volatile solvent with low solubility. As the highly soluble solvent continuously evaporates, the solubility of the polymer in the mixture gradually decreases, leading to phase separation. Vapor-induced precipitation involves introducing nonsolvent vapor into a polymer solution to induce phase separation. Immersion precipitation involves forming a thin layer of polymer dissolved in a high solubility solvent, followed by immersion in a non-solvent to induce phase separation and create porous materials. The main drawback of the NIPS method is that the resulting PU porous materials have small pore sizes, generally only 1 ~ 2 μm . Therefore, this method is often used in conjunction with other techniques. Gorna and Gogolewski (2006) combined NIPS with sodium phosphate salting leaching-phase inverse process to produce PU porous materials with a porosity of 90 % and an average pore size above 135 μm .

3.2.3. Gas foaming

The gas foaming technique is one of the most widely used methods for producing PU porous materials in industry and can be divided into chemical foaming and physical foaming methods. Chemical foaming involves adding substances that can undergo a chemical reaction with the polymer or undergo thermal degradation to produce gas, resulting in the formation of porous materials. Currently, most commercial PU foam products are produced using the chemical foaming method. Physical foaming involves pressurizing melt polymer with gases such as N_2 , CO_2 , or low-boiling-point alkanes to produce large-pore PU porous materials (Di Maio et al., 2005). The gas foaming technique does not require the use of organic solvents and is environmentally friendly. However, this method still has drawbacks such as difficulties in controlling pore size and distribution.

3.2.4. 3D printing

Rapid prototyping and manufacturing are a significant breakthrough in the field of manufacturing technology in recent decades, garnering widespread attention. In recent years, 3D printing technology has emerged as a prominent branch (Furet et al., 2019, Herzberger et al., 2019, Mauriello et al., 2023). 3D printing involves constructing a digital model using a computer and using layer-by-layer construction techniques to create the desired shape from a powdered adhesive material. Bates et al. (2016) used 3D printing technology to produce PU porous materials with honeycomb structures, enabling to create resilient architectures specifically tailored to operating applications and environmental conditions.

4. Superhydrophobic modification of PU porous materials

Pure PU foam exhibits high adsorption capacity for both oil, water and their mixtures, which greatly limits its application in the field of oil-water separation. Enhancing the hydrophobicity of materials and reducing their hydrophilicity is critical for efficient oil separation from water/oil mixtures (Abu-Thabit et al., 2022, Lu et al., 2022, Zhao et al., 2022). Therefore, it is necessary to modify the surface of PU foam. As shown in Fig. 3, the researchers modified the PU foam to enhance its superhydrophobicity through the synergistic effect of increasing surface roughness and reducing surface energy.

4.1. Increasing surface roughness

The methods of increasing the surface roughness of PU can be divided into two categories according to their mechanism: surface modification with nanoparticles and physical processing to increase the intrinsic roughness of the foam.

4.1.1. Nanoparticle modification

Nanoparticles are commonly used to increase the surface roughness of PU substrates. So far, carbon, magnetic Fe_3O_4 , and SiO_2 nanomaterials have been introduced to the surface of PU foam through dip-coating method (Anju and Renuka, 2020, Chen et al., 2020, Wang and Lin, 2013, Xu et al., 2015, Ye et al., 2020). For example, Xu et al. (2015) prepared superhydrophilic and superoleophobic PU sponges by a facile dip-coating a mixture of SiO_2 NPs and heptadecafluorononanoic acid-modified TiO_2 sol (HFA- TiO_2), exhibiting excellent performance in the selective removal of water from bulk oils. Wang and Lin (2013) dip-coated carbon nanotubes (CNTs) and polydimethylsiloxane (PDMS) onto PU foam, creating a robust superhydrophobic/superoleophilic material. This material can be used for continuous oil absorption and, in a vacuum system, can absorb oil up to 35,000 times its own weight.

Carbon nanomaterials as examples to provide a detailed introduction. They can aggregate to form rough micro/nano-scale structures, which are widely used for constructing superhydrophobic surfaces. For example, carbon nanotubes are often used to create superhydrophobic surfaces due to their inherent hydrophobicity, high adsorption capacity, low density, and excellent mechanical properties. As shown in Fig. 4A, PU could be modified with MWCNT through hydrogen bond or π - π interaction. (Juraj et al., 2022) As shown in Fig. 4B, Ye et al. (2020) utilized hydrophobic carboxyl multi-walled carbon nanotubes (cMWNs) and TPU to manufacture a robust hybrid sponge via the TIPS method. The addition of 2 % cMWNs resulted in a WCA of 151°.

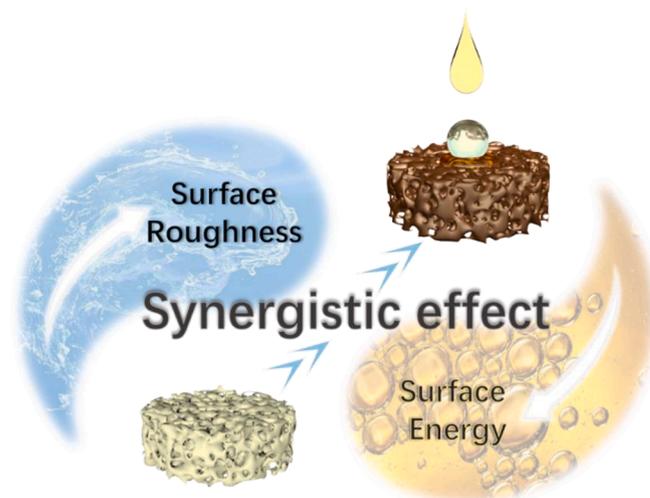


Fig. 3. Strategies to achieve superhydrophobic modification through the synergistic effect of increasing surface roughness and reducing surface energy.

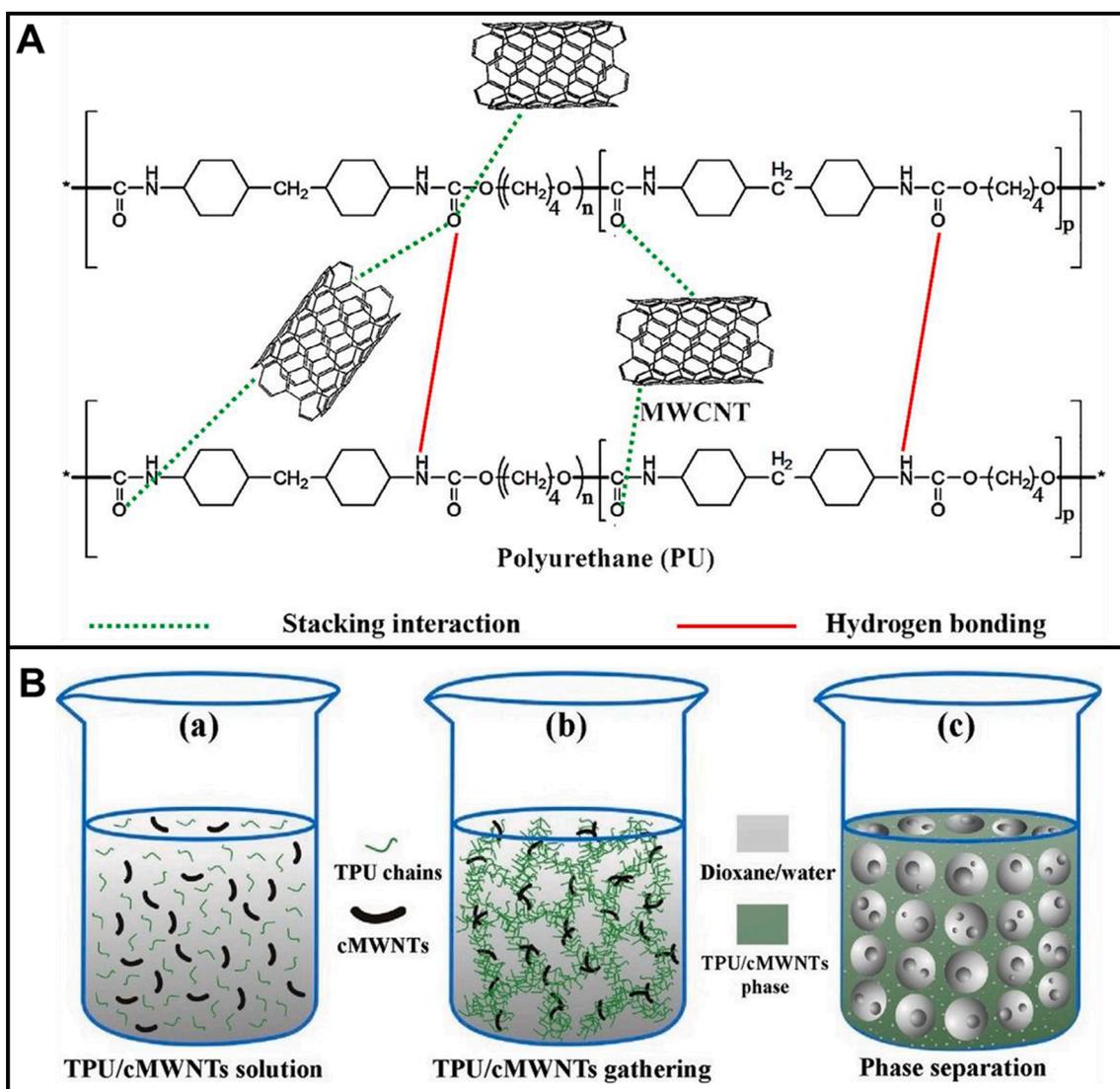


Fig. 4. (A) The interaction between multi-walled carbon nanotube (MWCNT) and PU through hydrogen bond and π - π interaction. (B) Schematic diagram of the preparation procedure of superhydrophobic TPU/cMWNTs. Adapted and modified from Juraij et al. (2022) and Ye et al. (2020).

exhibiting an absorption capacity ranging from 6.9 to 42.3 (g/g) for different oils and organic solvents. Even after 40 cycles, the separation efficiency for soybean oil remained above 98 %. Furthermore, the TPU/cMWNTs nanohybrid material retained good elasticity after 1000 compression cycles and can be recycled using a simple compression recovery method. Chen et al. (2020) used hydroxylated MWCNTs by condensing them with long-chain hexadecyl siloxane, then incorporated these MWCNTs-OH into PU sponge through an immersion coating process. This resulted in a superhydrophobic MWCNTs@PU nanohybrid sponge for selective oil-water separation, with a WCA of $157.4 \pm 1.1^\circ$ and water droplets roll-off angle of 6.7° , displaying effective adsorption for various oils and organic solvents.

In addition, by introducing a variety of particle modifications, more functional hydrophobic PU porous materials can be obtained. A typical example is incorporating magnetic nanoparticles. Anju and Renuka (2020) prepared graphene-mesoporous Fe_3O_4 composite materials by loading Fe_3O_4 onto graphene and incorporating it into PU foam for modification. The material exhibited a WCA of 151° and maintained oil adsorption capacities between 90 and 316 (g/g) for different types of oil. The Fe_3O_4 not only increased surface roughness but also stored oil within its pores, enhancing the maximum adsorption capacity of the PU foam. Leveraging its magnetism, Fe_3O_4 facilitated the electrostatic

attraction of oil or other organic solvents, further enhancing oil adsorption.

4.1.2. Physical processing

Etching, laser ablation, plasma treatment, and other physical methods can be used to increase surface roughness or generate micro/nano hydrophobic structures on the substrate surface. Etching is a technique that increases roughness by removing material from the surface and is often employed before coating with low surface energy molecules (Abu-Thabit et al., 2022, Liu et al., 2015, Yang et al., 2023). Traditional methods typically involve the use of corrosive or reactive chemicals, such as concentrated acids or bases at elevated temperatures, to etch the substrate surface. Other methods include sanding the surface. As shown in Fig. 5, Yang et al. (2023) firstly etched original PU sponge by immersing it in $\text{CrO}_3/\text{H}_2\text{SO}_4$ and then coated the surface to get enough surface area. The etching process increases surface roughness and produces hydrophilic groups such as $-\text{COOH}$ and $-\text{OH}$, which can promote the binding of Ni-Co double-layer oxide nanoparticles on the surface. After modification with n-dodecyl mercaptan, it can produce a WCA of 157° and selectively absorb oil.

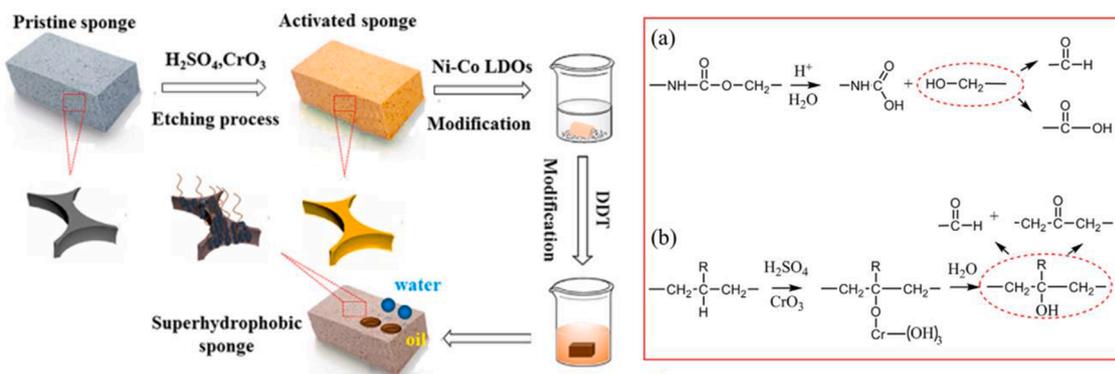


Fig. 5. Schematic diagram of synthesis process of superhydrophobic PU sponge including etching process. Adapted and modified from Yang et al. (2023).

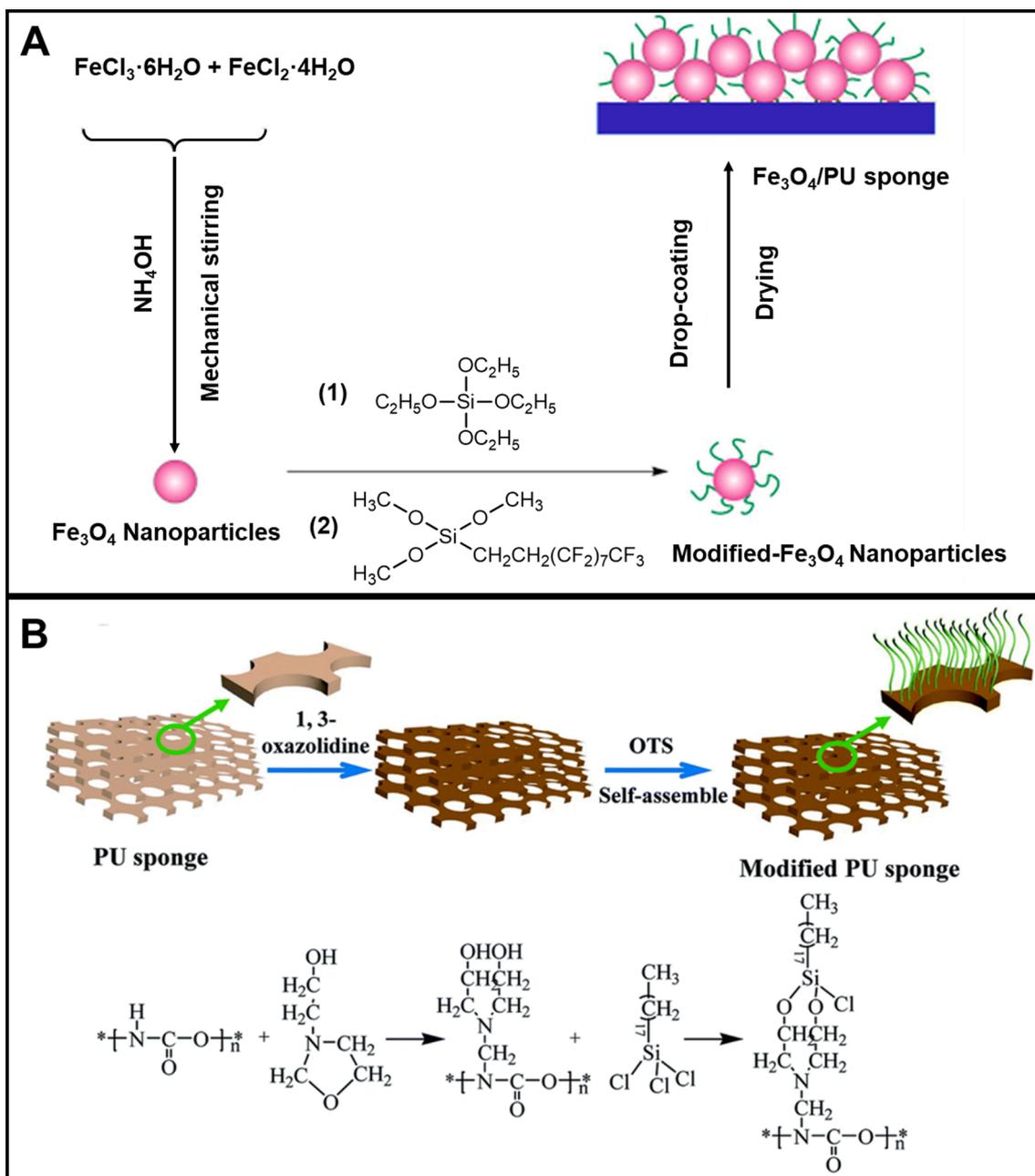


Fig. 6. (A) Schematic diagram of the preparation of superhydrophobic $\text{Fe}_3\text{O}_4/\text{PU}$ sponge. (B) Schematic diagram of the modification process of PU using octadecyltrichlorosilane (OTS). Adapted and modified from Li et al. (2018) and Liang et al. (2019).

4.2. Reducing surface energy

Another common method to enhance the hydrophobicity of PU foam is to coat the surface with low surface energy substances. Currently, such functional substances can be divided into carbon-based materials, organosilanes, thermoplastic polymers, conductive polymers and long alkyl chains according to their inherent properties.

4.2.1. Organosilane modification

Organosilane materials possess low surface energy, and their functional groups (e.g., Si-Cl, Si-NH-Si, Si-OCH₃, and Si-OCH₂CH₃) hydrolyze into silanol groups. These silanol groups can couple with the hydroxyl groups on the PU substrate, forming a hydrophobic coating, making them widely used for superhydrophobic modification. (Lu et al., 2015).

As shown in Fig. 6A, Li et al. (2018) modified PU using Fe₃O₄ NPs, trimethoxy (1H,1H,2H,2H-heptafluorodecyl) silane (TMHFDS), and tetraethoxysilane (TEOS) through a drop-coating method, resulting in a low surface energy magnetic sponge with a WCA of 154.7°. They conducted quantitative oil–water separation tests using peanut oil, pump oil, and silicone oil, showing absorption capacities ranged from 4 to 46.3 (g/g). As shown in Fig. 6B, Liang et al. (2019) utilized OTS modification, where long-chain OTS molecules with —CH₃ terminal groups self-assembled onto the hydroxyl groups of PU, successfully producing PU sponges with excellent oil–water separation performance. This material exhibited adsorption capacities for various oils or organic solvents ranging from 20 to 25 times its own weight. Furthermore, it demonstrated outstanding oil retention with an oil retention rate of up to 92.6 %, effectively preventing oil detachment and enabling recyclable oil pollution cleanup.

4.2.2. Polymer modification

Although nanoparticle modification strategies can achieve most oil–water separation applications in immiscible and emulsion applications, many performance results are unsatisfactory due to their larger pore sizes. In addition, due to the large number of oil droplets embedded in the skeleton, the material surface is also easily contaminated, resulting in a decrease in separation performance. The polymer layer modification can reduce the pore size of the PU foam and provide huge active surfaces and functional groups for the modified nanoparticles to be embedded (Cheng et al., 2018, Khosravi and Azizian, 2015, Satria

and Saleh, 2023, Yu et al., 2019). This strategy results in a rougher surface, more superhydrophobicity, and stronger binding between PU foam and modified nanoparticles, resulting in consistently high performance in practical applications.

One approach involves modifying polyethylene (PE) sponge using hydrophobic thermoplastic polymers such as polypropylene (PP), polystyrene (PS), and polyvinyl chloride (PVC). They have often been used to create low surface energy coatings on the surface of PU. As depicted in Fig. 7, Cheng et al. (2018) reported the preparation of superhydrophobic PU coated with HDPE using a drop casting method at room temperature. They used xylene as a solvent and ethanol as a non-solvent. The resulting sponge exhibited oil absorption capacities ranging from 32 to 90 (g/g) for different types of oil and maintained stable performance over 10 separation cycles. Due to the presence of the HDPE coating, the prepared sponge exhibited excellent chemical stability across a pH range of 1–14. Yu et al. (2020) developed magnetic superhydrophobic PU using different methods. They utilized Fe₃O₄ magnetic NPs to increase surface roughness and coated them with HDPE as a low surface energy hydrophobic layer. The resulting sponge displayed oil adsorption capacities ranging from 15 to 52 (g/g) for various oils and demonstrated good chemical stability in both acidic and alkaline environments. Experimental validation confirmed that this sponge exhibited persistent oil-absorbing capabilities below the melting point of HDPE (130 °C).

The other is to use conductive polymers, such as polyaniline (PANI), polypyrrole (PPy), and polythiophene (PT), to enhance the oil–water separation performance of PU pore materials (Khosravi and Azizian, 2015, Li et al., 2020b, Satria and Saleh, 2023). Among various conductive polymers, PANI exhibits excellent chemical and mechanical durability, making it one of the promising materials for modifying PU. Li et al. (2020b) used low surface energy fluorocarbon as a doping acid and synergistically interacted it with the layered micro/nanoscale structures of densely grown PANI nanofibers to modify PU sponges into superhydrophobic materials suitable for oil–water separation. The modified PU material achieved a WCA of 150°, exhibited absorption capacities ranging from 44 to 95 (g/g) for different oils and organic solvents, maintained stable performance over 20 separation cycles, and demonstrated good chemical stability in acidic, saline, corrosive environments, as well as in hot water at temperatures up to 70 °C.

As illustrated in Fig. 8, Zhang et al. (2016) utilized 1,3,5-benzenetri-carbonyl trichloride (TMC) as the oil-phase monomer and ethoxylated

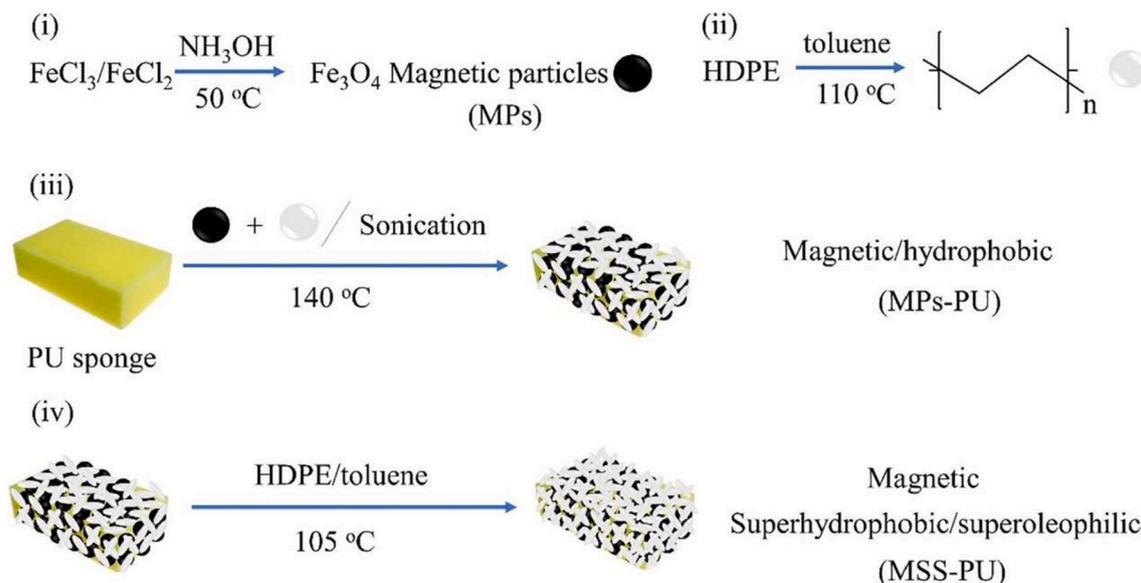


Fig. 7. Schematic diagram of the preparation of superhydrophobic PU coated with high-density polyethylene (HDPE). Adapted and modified from Cheng et al. (2018).

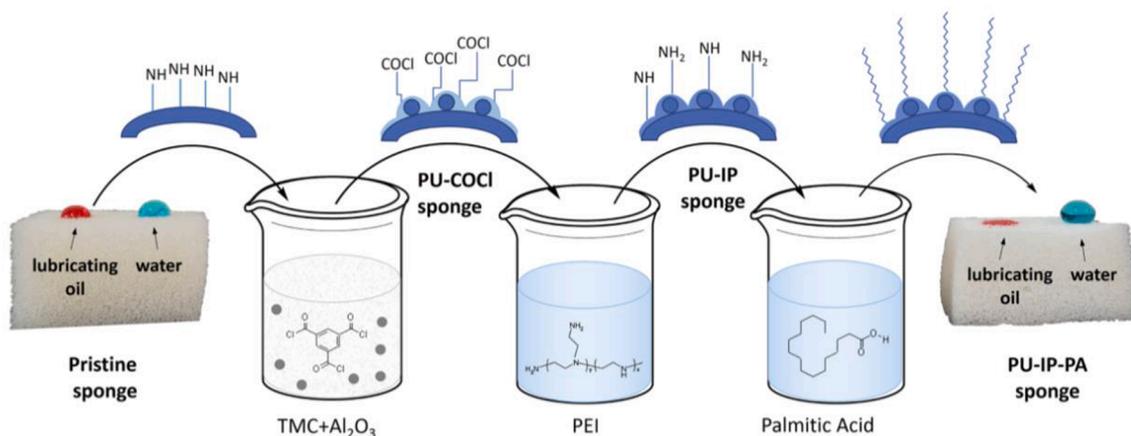


Fig. 8. Schematic diagram of the fabrication process of PU-interfacial polymerization -palmitic acid (PU-IP-PA) sponge. Adapted and modified from Zhang et al. (2016).

polyethyleneimine (PEI) as the aqueous-phase monomer, through a combined IP and molecular self-assembly method, a dense membrane was formed. Due to TMC's facile reaction with the secondary amine of PU sponge, the resulting membrane was firmly adhered to the sponge surface through covalent bonds, providing excellent stability and durability. The produced sponge demonstrated extremely high reusability in oil-water separation applications, maintaining its superhydrophobicity even after over 500 repeated uses.

4.2.3. Long alkyl chain compound modification

Coating a PU substrate with long alkyl chains can significantly reduce the material's surface energy, imparting strong hydrophobicity to the base material (Abu-Thabit et al., 2022, Han et al., 2011, Li et al., 2019). Therefore, derivatives of long alkyl chains, such as fatty acids (Chhajed et al., 2023, Liu et al., 2011), alkylthiols (Li et al., 2012, Wang et al., 2013), and alkylamines (Li et al., 2020a), are often used to create superhydrophobic surface coatings on PU materials.

As shown in Fig. 9, Tran and Lee (2017) utilized an immersion coating method to manufacture PU foam coated with Fe_3O_4 and ZnO NPs along with stearic acid. The resulting PU@ZnO@SA@ Fe_3O_4 nanocomposite sponge achieved a WCA of 161° and could be used to remove various oils and organic solvents, with a maximum adsorption capacity of 109 (g/g) and a separation efficiency of up to 99.9%. Sun et al. (2021) reported the preparation of PU foam coated with ZnO NPs/epoxy resin/stearic acid using an immersion coating method. Results indicated that after five repeated coatings, the sponge with the WCA of $158 \pm 1.9^\circ$ was tested for the separation of different oils and organic solvents and maintained a separation efficiency above 97% even after 10 cycles of separation.

5. Superhydrophobic modification of PU porous materials

Superamphiphobic (superhydrophobic and superoleophobic) materials have attracted much attention for its wide applications including water-oil separation (Liu et al., 2018). Because superhydrophobic/superoleophobic materials (Chen et al., 2019a) is not suitable for light oil-water separation ($\rho_{\text{water}} > \rho_{\text{oil}}$) by gravity, and superhydrophilic/underwater superoleophobic materials are not suitable heavy oil-water separation ($\rho_{\text{oil}} > \rho_{\text{water}}$). Furthermore, the surface energy of oil is usually much lower than that of water, and most superhydrophobic materials do not always repel oil and can easily lose wettability due to oil contamination in the air. Therefore, superamphiphobic materials are highly desirable, especially those that can realize on-demand oil-water separation by prewetting method (Ge et al., 2015; Xu et al., 2015).

To date, many methods have been developed to prepare superamphiphobic surfaces (Chen et al., 2019b; Gu et al., 2020b; Zhou et al., 2013). Those methods can be divided into two types. One is dry physical methods, such as plasma etching, photolithography and 3D printing. The other is wet chemical methods, such as coating, hydrothermal and solvothermal methods. Among them, silica-containing coating is the most common and most common and simplest wet chemical techniques to fabricate superamphiphobic surfaces. For example, Zhang et al. prepared a stock suspension consist of siliconemodified polyurethane (Si-PU) adhesive containing fluorinated silica (FD-silica) nanoparticles via nonsolvent-induced phase separation (Zhang et al., 2022a). As shown in Fig. 10A, it can be easily used for a facile fabrication of robust superamphiphobic coatings on various substrates ranging from metals (Al, Mg, Cu) to inorganic oxides (glass and ceramic), synthetic polymers (PP and PET) and natural wood.

Furthermore, these as-prepared superamphiphilic composites show

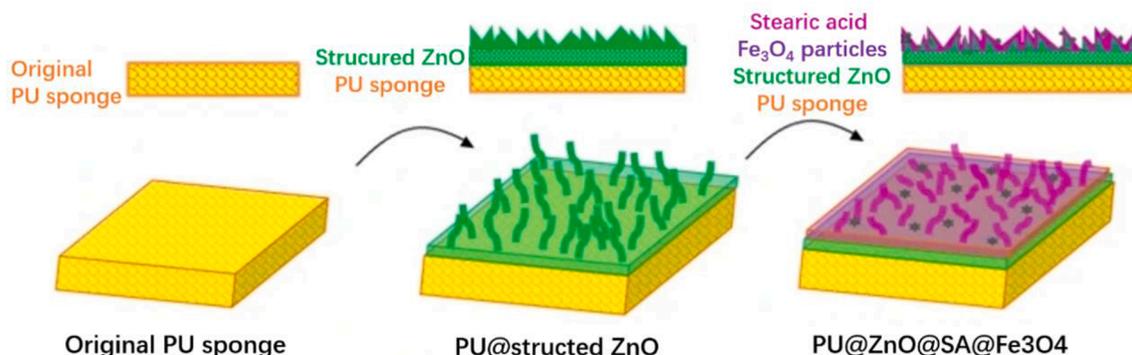


Fig. 9. Schematic diagram of the modification of PU foam coated with Fe_3O_4 and ZnO NPs along with stearic acid. Adapted and modified from Tran and Lee (2017).

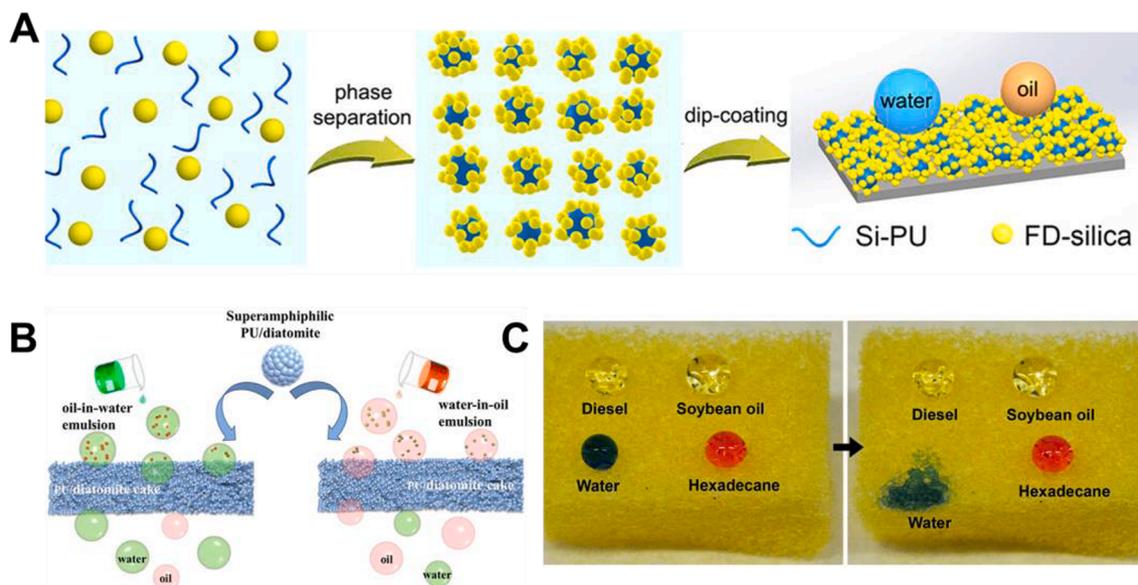


Fig. 10. (A) Schematic illustration of the FD-silica/Si-PU superamphiphobic coatings. (B) Schematic diagram of a superamphiphilic porous composite of diatomite and PU was used for the coalescence demulsification of oil-in-water and water-in-oil emulsions with and without a surfactant. (C). Photos of water and oil droplets placed on the superamphiphilic PU sponge before and after ammonia exposure. Adapted and modified from Zhang et al. (2022a), Wu et al. (2022), and Xu et al. (2015).

unusual capabilities for controllable oil–water separations (Liu et al., 2022; Wu et al., 2022; Xu et al., 2015). For example, as shown in Fig. 10B the as-prepared superamphiphilic polyurethane (PU)/diatomite composite can be used to effectively demulsify kerosene-in-water and water-in-kerosene emulsions with and without a surfactant (Wu et al., 2022). Then combining a superhydrophobic channel for separation, the oil–water separation efficiency exceeds 99.0%, to get qualified oil and water. Xu et al. used a mixture of silica nanoparticles and heptadecafluorononanoic acid-modified TiO_2 sol a superamphiphobic coating that turns superhydrophilic and superoleophobic upon ammonia exposure (Xu et al., 2015). As shown in Fig. 10C the coating-functionalized PU sponge can significantly change its wettability to absorption of water after ammonia exposure. These novel coatings can lead to the development of advanced oil–water separation techniques, which can be used for on-demand oil–water separation with high separation efficiency and outstanding reusability.

6. Recyclability

PU is highly stable mechanically and chemically, making them resistant to natural degradation and posing significant environmental challenges when discarded. In addition, due to the scarcity of petroleum resources, the maximum recovery and reuse of petroleum and PU materials after oil–water separation is of great significance for environmental protection and cost reduction. Therefore, the recyclability of materials is a key aspect to comprehensively evaluate the oil–water separation performance of porous PU materials. We summarize the common methods for the recycling of oil-absorbing materials, and compare their applicability and operational feasibility of porous PU materials for oil–water separation.

6.1. Combustion method

The combustion method involves directly igniting porous materials that have absorbed combustible oils. This method not only utilizes the energy content of energy-rich oil substances but also recycles and reuses the oil-absorbing materials. Combustion recovery is primarily dependent on the combustibility of the absorbed oils and the stability of the physical and chemical properties of porous materials at high

temperatures. This method requires the materials to maintain hydrophobicity and structural strength under elevated temperatures.

Due to the flammability of aliphatic segments and porous structure of PU, it burns quickly, which limits its recycling and reuse using the combustion method. In order to make PU a flame-retardant superhydrophobic adsorbent, a variety of chemicals have been used to functionalize it, such as inorganic nanoparticles, organophosphorus compounds and carbon nanomaterials (Patra et al., 2014; Wang et al., 2022; Ji et al., 2017; Lee et al., 2019; Mehrdad and Taleb-Abbasi, 2016; Xin et al., 2017). For example, as schematically illustrated in Fig. 11A, Zhou et al. (2022) prepared FeOOH modified flexible PU foam through a simple hydrothermal method, which greatly improved the hydrophobicity, lipophilicity, and flame-retardant properties. Jamsaz and Goharshadi (2020) functionalized PU with reduced graphene oxide (RGO) and o-aminophenol (OAP), the possible molecular interactions of which are shown in Fig. 11B, the RGO/OAP/PU sponge exhibited superhydrophobicity, with a WCA of $179 \pm 0.35^\circ$, which remained unchanged after a 60 s burning test with a little change in its infrared spectra.

However, oil combustion produces many combustion residues, which may have an impact on the superhydrophobicity of porous materials. Therefore, the use of combustion method to recover oil-absorbing materials has great limitations, and it is easy to cause secondary pollution. Due to the flammability of PU itself, although many methods have been used to improve it, it is currently difficult to make it reusable through combustion recycling.

6.2. Squeezing method

This recycling method involves using external compressive force to physically squeeze absorbed oil from porous materials. Typically, this requires porous materials that are superhydrophobic and superoleophilic, allowing for highly selective oil absorption; In addition, it is also required that the adsorption material has good elasticity to maintain its structure and performance in repeated extrusion.

As PU sponge has excellent flexibility, its microstructure is not easily affected by external force; While PU can adsorb both oils and water, thus it is essential to change the hydrophilicity of sponges to superhydrophobicity and superoleophilicity for practical application of

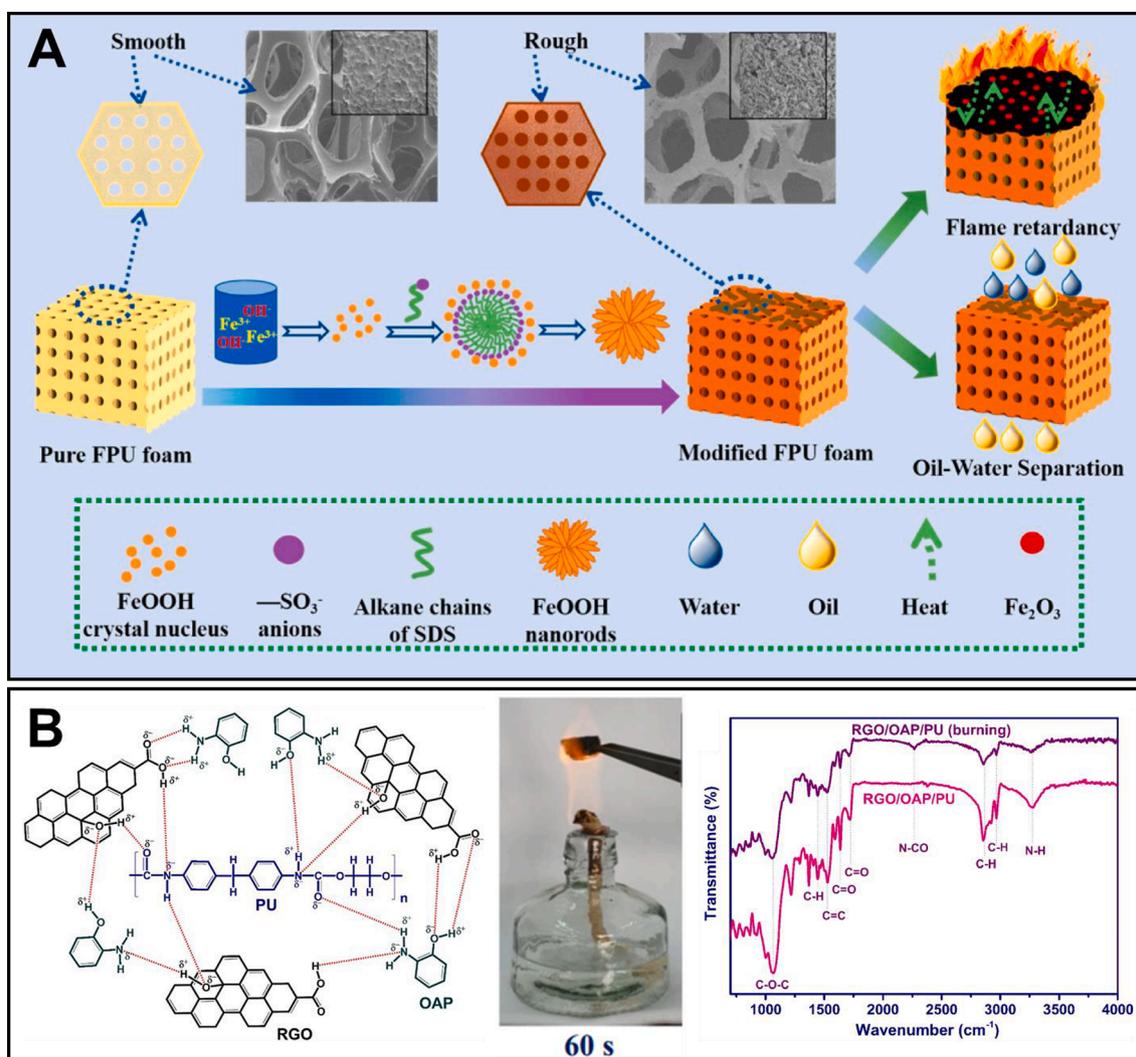


Fig. 11. (A) Schematic diagram of the fabrication of FeOOH modified flexible PU foam with good flame-retardant property. (B) Schematic diagram of the possible interactions in RGO/OAP/PU sponge, photo of flammability test, and FTIR spectra of RGO/OAP/PU sponge. Adapted and modified from Zhou et al. (2022) and Jamsaz and Goharshadi (2020).

oil–water separation. As schematically shown in Fig. 12A, the superoleophilic sponge can easily remove and collect oil in water through a simple mechanical squeezing process (Zhu et al., 2011). Fig. 12B shows that the TPU monolithic material manufactured by the thermally induced phase separation method exhibits significant superelasticity (Qin et al., 2019), reversible compressibility and excellent fatigue resistance after 1500 cycles under a large strain of 80 %. These advantages allow it to a good reusability and recyclability in oil–water separation through the manual squeezing method.

The squeezing method is a direct oil recovery method with low equipment requirements and environmental friendliness. The excellent elasticity of the porous material allows it to return to its original state after extrusion, which is conducive to repeated oil absorption and recycling. This method preserves the original properties of the absorbed oil, but is less effective for oils with higher viscosity.

6.3. Distillation method

The distillation method is to heat the oil-absorbing porous material to evaporate the adsorbed oil, and then collect the oil through reflux condensation to restore the adsorption capacity of the porous material for recycling. As schematically shown in the Fig. 13, the hydrophobic and lipophilic sponges first selectively adsorb the oil in the mixture and

then transfer it to the distillation vessel (Bi et al., 2012). The temperature can be controlled and maintained near the boiling point of the absorbent for vaporization. Absorbed organics are released by simply heating the material and collecting condensate, with no combustion or structural damage occurring during heat treatment at moderate temperatures. Therefore, many pollutants, including heavy oils, can in principle be separated after thermal treatment and further reused. This method can directly fractionate crude oil at different temperatures during the distillation recovery process, thereby enhancing the applicability of the recovered products.

6.4. Pump-assisted continuous absorption method

The pumping-assisted continuous absorption method involves installing a pump unit alongside the oil-absorbing porous hydrophobic material (Qin et al., 2019, Zhou et al., 2018). As shown in Fig. 14, the pump is used to extract the absorbed oil from the porous material, restoring its adsorption capacity and facilitating continuous oil-absorbing operations (Shi et al., 2021). Extracting oil from porous materials requires a continuous extrusion process. PU-based porous materials have excellent superelasticity, reversible compressibility and excellent fatigue resistance, showing a great potential as the sustainable absorbent materials for the cleanup and recycling of oil and organic

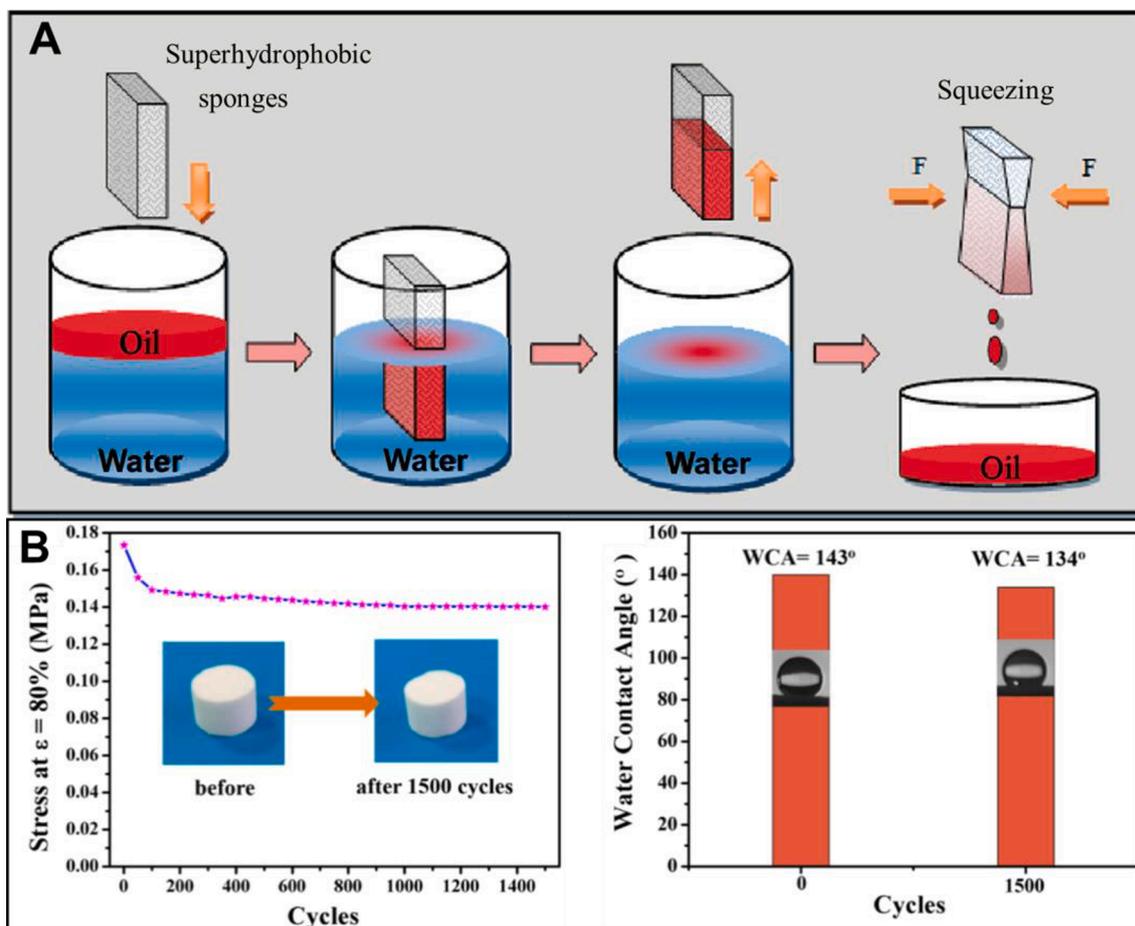


Fig. 12. (A) Schematic illustration of recycling superoleophilic sponge during oil-water separation by simple mechanical extrusion process. (B) Compressive stress of TPU sponge after 1500 cycles and its WCA before and after compression. Adapted and modified from Zhu et al. (2011) and Qin et al. (2019).

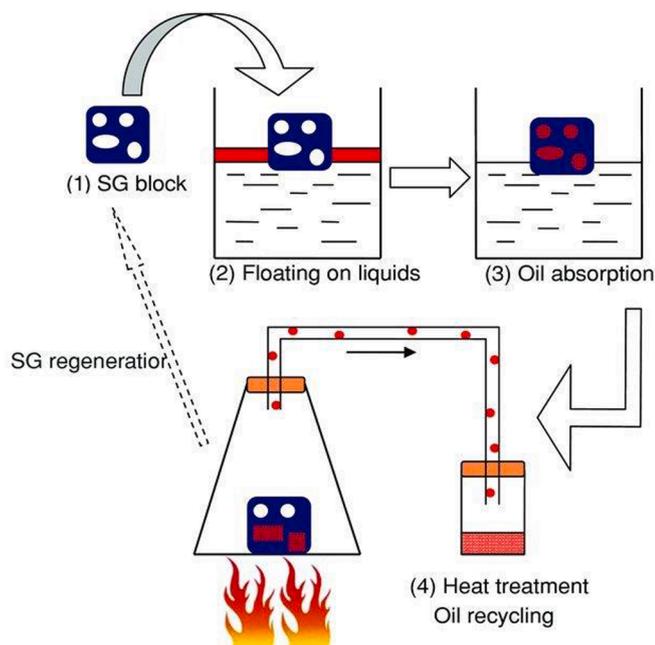


Fig. 13. Schematic diagram of distillation recovery method. Adapted and modified from Bi et al. (2012).

solvent pollutions. For example, Qin et al. have proven that that porous TPU monoliths have been shown to continuously separate at least 4500 times their own weight in oil/organic solvents using a pump-assisted continuous absorption system (Qin et al., 2019). Therefore, this method has broad application prospects in dealing with large-scale water surface oil spills.

6.5. Self-healing method

To improve the long-term performance in continuous oil-water separation, scientists recently have synthesized many self-healing polyurethanes with excellent dynamic chemical bonds (Chen et al., 2019a; Liu et al., 2022; Mao et al., 2023b), such as hydrogen bonds, metal coordination bonds, nanofiller combined dynamic covalent bonds and multiple dynamic covalent bonds (An et al., 2023; Sai et al., 2022). Among them, a self-healable waterborne polyurethane coating has been deposited onto different substrates through a simple soaking procedure for high-efficiency oil/water separation.

For example, Mao et al. integrated disulfide groups into waterborne organic silicone polyurethane and then coated it on cotton fabrics (Fig. 15A), which still showed high superhydrophobic properties even after 80 washes or 800 wears (Mao et al., 2023b). The damaged surface could heal itself up to 90.8 % by heating it at 80°C for half an hour due to the dynamic reversible reaction of the hydrogen bond and disulfide bond (Fig. 15B). Chen et al. used a pH-responsive polyurethane and fluorated octavinyl polyhedral oligomeric silsesquioxane to fabricate durable UV-cured smart fabric coatings with self-cleaning and pH-controllable oil/water separating ability (Chen et al., 2019b). The protonation and deprotonation of pH-PU resins lead to the switchable

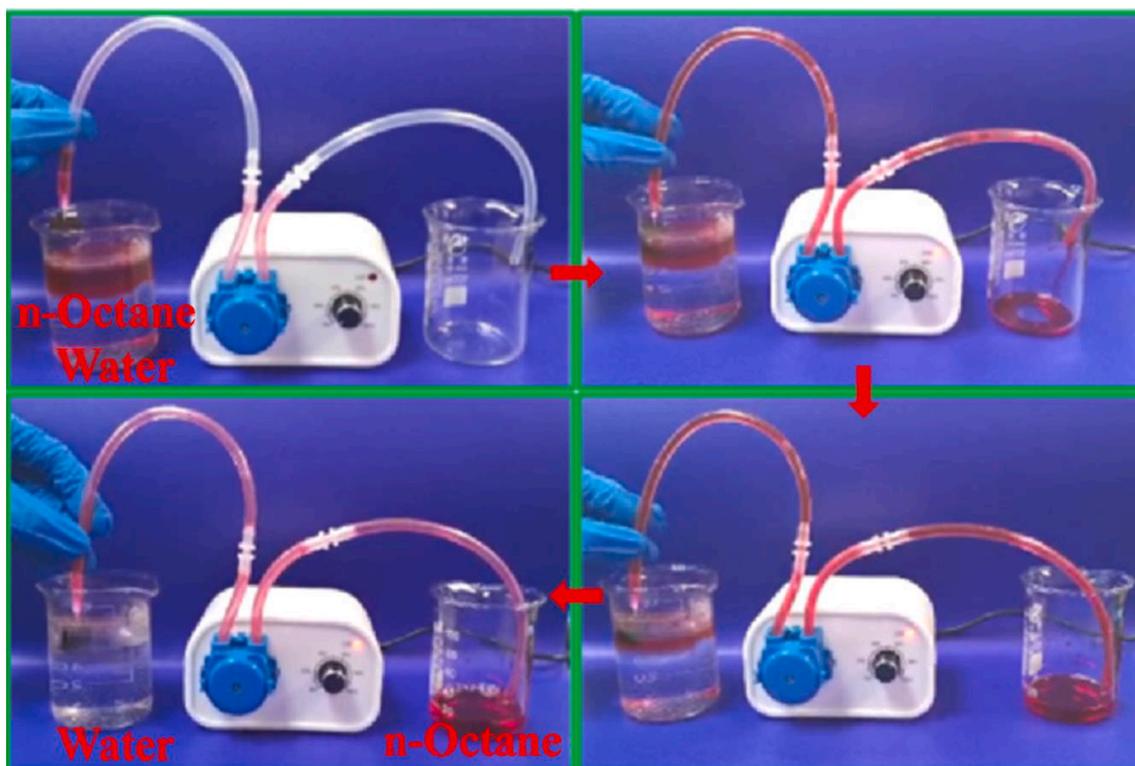


Fig. 14. Pump-assisted continuous separation process of oil–water mixture. Adapted and modified from Shi et al. (2021).

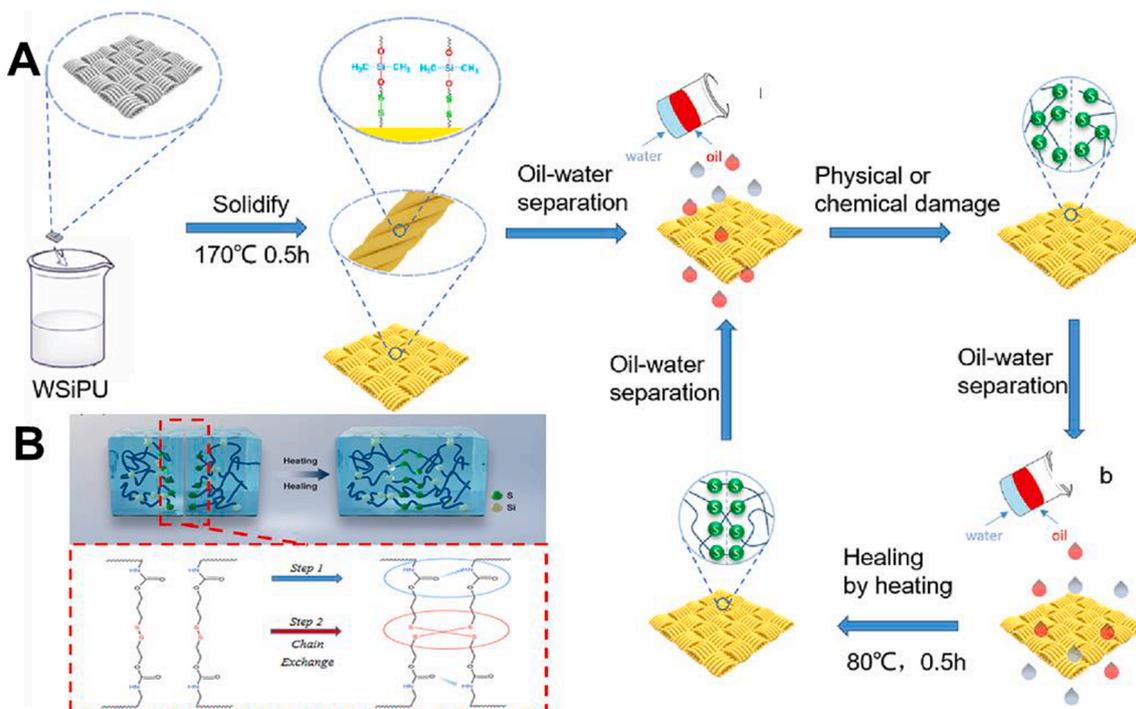


Fig. 15. (A) Schematic diagram of the self-healable coating using Waterborne organic silicone polyurethane for oil–water separation. (B) The proposed mechanism of self-healing. Adapted and modified from Mao et al. (2023b).

wettability from superhydrophobicity to underwater superoleophobicity upon changing pH. Furthermore, it could restore their special wettability by migrating the fluorocarbon chains to the outer surface of coatings through simply heating. Thus, the combination of superior self-healing ability and superhydrophobic properties provides a general approach for the long-term application in oil–water separating.

7. Conclusion and outlook

In summary, superhydrophobic/superoleophilic nanohybrid PU porous materials have been proven a promising class of selective oil absorbents for oil–water separation. To achieve good durability, oil recovery, and oil capacity, different preparation methods have been

developed to fabricate PU membranes and foams with different pore sizes, pore shapes, and porosity. Furthermore, the modification of organic and inorganic nanohybrid materials opens new horizons for the design of diverse and broad superhydrophobic/superoleophilic PU sponges due to the synergistic effect between chemical composition and surface roughness. These porous PU materials have great potential in cleaning oil pollution from water bodies.

However, there are still many challenges to overcome, such as unsatisfied oil capacity, efficiency, and reusability. Each method used to produce hydrophobic PU porous materials has certain limitations. For example, poor adhesion between modification layers and substrates leading to low reusability of materials, hinder the practical application of these materials. Therefore, current research directions include improving the manufacturing process and integrating the advantages of different preparation methods to minimize limitations in the practical application of porous PU materials. It is designed to meet the requirements of mass production, low raw material cost, simple process and good reusability. At the same time, it is also crucial to enhance the stability of PU-based materials in complex environments (such as strong acid, strong alkali, and salt environments).

In addition, the current testing method for oil–water separability of porous PU materials is relatively simple. Qualitative and quantitative studies on the interaction between the solid/liquid interface on the surface of PU materials and the oil–water mixture are also needed to provide targeted guidance for the development of new materials. Therefore, over the past few decades, there have been numerous research reports analyzing the performance of PU 3D porous materials in oil/water separation applications. Research usually uses low-viscosity light oil or organic solvents as simulated pollutants for oil–water separation tests. However, real-world oil contamination often involves high-viscosity crude oils, so improving material properties to make them suitable for effective cleaning of high-viscosity oils remains of critical practical significance.

To overcome the above-mentioned shortcomings and the wide variety and complexity of oil spills, chemical releases and wastewater, intensive efforts are being made to develop smart surfaces with tunable and switchable wettability for oil/water separation (Deng et al., 2021; Liu et al., 2022). In particular, the smart separating membranes with switchable responsive wetting state are capable of water-removal and oil-removal processes upon external triggers like pH, light, temperature, gas, solvent, electricity and so on (Han et al., 2022; Yu et al., 2023; Zhang et al., 2021). Owing to the effective separation performance and good recyclability, the wettability-regulated separating techniques display great advantages over traditional separating technique. These smart wettability materials have a promising application potential in controllable oil–water separation and on-demand oil-spills treatment.

CRedit authorship contribution statement

Zhen-Wei Yang: Conceptualization, Resources, Writing – original draft. **Jia-Jie Li:** Data curation, Formal analysis, Writing – original draft. **Zhou Yu:** Data curation, Writing – original draft. **Ju-Fang Zheng:** Conceptualization, Validation, Writing – original draft. **Ya-Hao Wang:** Conceptualization, Funding acquisition, Project administration, Supervision, Writing – review & editing. **Xiao-Shun Zhou:** Funding acquisition, Project administration, Supervision, Validation, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

The authors gratefully acknowledge financial support from the Zhejiang Provincial Natural Science Foundation of China (no. LQ21B030010) and National Natural Science Foundation of China (nos. 22102150, 22172146, 21872126 and 21573198).

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