Surface modification of polypyrrole-coated foam for the capture of organic solvents and oils

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Abstract The low stability and complicated fabrication procedures seriously hindered practical applications of superhydrophobic and superoleophilic materials. Here, we present a simple method for preparing the novelly three-dimensional material based on commercially available nickel foams functionalized with electrodepositing of sub-micrometer polypyrrole (PPy) particles, followed by modification of low-surface-energy material such as fluoroalkylsilane (FAS), which can efficiently separate oils and organic solvents from water. The formation of nanostructured surface roughness of PPy onto the nickel foam by combination with FAS modification would contribute to the excellent superhydrophobic and superoleophilic performance, as is the evidence of the water CA of 155° and oil CA of ca. 0° for FAS-treated PPy foam. As a separating membrane, organic solvents and oils could be easily removed without obvious absorption of water, which has great potential over traditional treatment techniques and is of technological significance as a promising and efficient absorbent material for separation of organic contaminates and oils from water.

Introduction

The pollution of groundwater and seawater has become a severely environmental hazard as the result of oil spillage and industrial waste such as chemicals and pesticides [1]. To address environmental issues, such development of novel strategies with high separation capacity, high selectivity, and stable performance for removal of oil spillage or industrial contaminants should be of significant importance and urgently needed. So far, many conventional methods such as gravity separation, ultrasonic separation, and absorption technology [2–6] have been widely used in application of oils (organics)/ water separation. Among absorbent materials, many kinds of superwetting materials such as sponges [7–10], superhydrophobic graphene [11–20], carbons [21–23], superwetting inorganic (organic) nanowire membranes [24–30], microporous polymers [31], and macroporous gels [32–34] et al. have been reported to have excellent absorption selectivity for removal of organics and oils from water [8, 35–37]. The first case of oils/water separation has been reported by Jiang and coworkers [2] using a mesh with coating of superoleophilic materials. Along this line, the creation of nanometer- or micrometer-sized porous materials with good superhydrophobic surface has more recently been demonstrated for successful use in the separation and absorption of oils and organic solvents from water. In our previous studies, we also reported the preparation of superhydrophobic polymer [38], microporous absorbents [39, 40], and mesh film [41] for removal of oils and organic solvents from water. Quite different from some traditional absorbents such as active carbon [42] and clay [43, 44], these superhydrophobic absorbents or meshes show excellent absorption selectivity, high absorbency and recyclability for oils (organics)/water separation. In most cases, the needing of complicated fabrication techniques is a major obstacle which hinders their large-scale practical application. Based on this point, the exploring of simple

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Fig. 1 a Schematic diagram: fabrication of PPy-coating nickel foam by electrodepositing method. b SEM image of pure nickel foam. Inset is higher magnification SEM of nickel foam surface. c SEM image of PPy foam. *Inset* is higher magnification SEM of PPy foam surface. *Scale bar* b 10 μm, c 10 μm
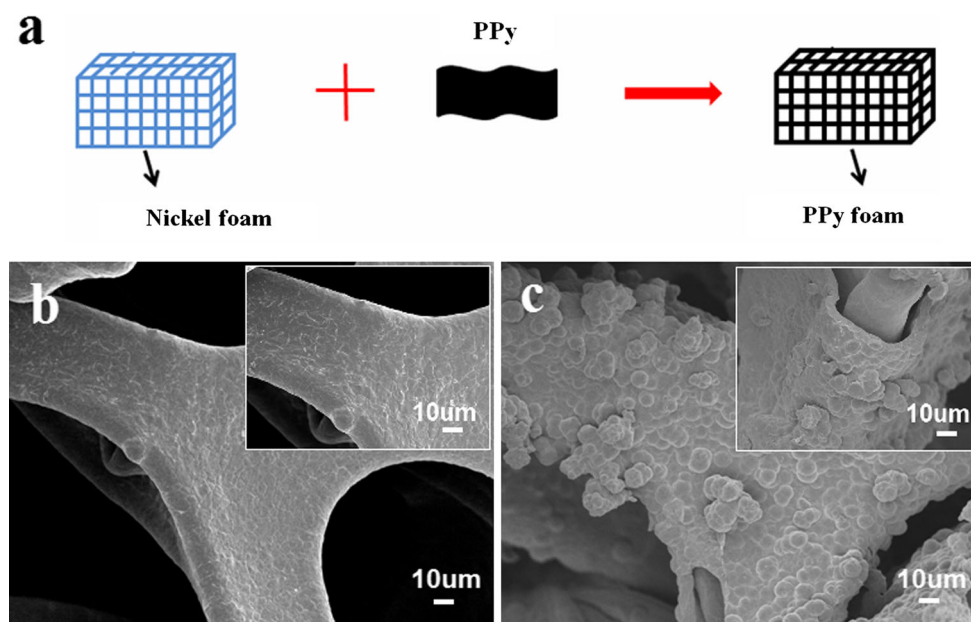
method for preparation of superwetting absorbents for oils (organics)/water separation should be of most importance to address this problem. In this work, the preparation of superhydrophobic and superoleophilic foam with simple coating of conductive polymer by electrodepositing method was reported, followed by modification with low-surface-energy material, such as fluoroalkylsilane (FAS), for organics/oils and water separation. As a membrane for oils (organics)/water separation, the oils, and organics can be continually removed from water with high absorption selectivity, which would have great potential in applications of water treatment and oil spillage cleanup, etc.

Experimental section

Preparation of PPy foam

Pyrrole (99 %, J&K) was purified and stored below 0 °C before using. Commercial nickel foam as working electrode was ultrasonic ion treated with aqueous NaOH (1 M), distilled water and ethanol, respectively. A plate of platinum (size: 15 mm × 15 mm × 0.2 mm) was used as counter electrode after being washed by HCl (1 M) and distilled water. The electrodepositing solution contained pyrrole (0.14 M) and SDBS (0.015 M) and 100 mL distilled water. A small amount of $NaClO_4$ (0.1 mg) was used as the oxidant during the electrodepositing process. PPy was obtained on the surface of nickel foam with two-electrode system at 11.5 V for 3 h (Fig. 1a). The resulted PPy foam was washed with distilled water, acetone and air-dried.

Surface modification

The resulted PPy foam was treated by dip-and-dry method, which was repeatedly dipped into a FAS/toluene solution (3 wt%) and dried in an oven at 80 °C for 12 h.

Characterization

The morphology of the PPy foam was measured by scanning electron microscopy (SEM, JSM-7601F). Solid Fourier transform infrared spectra (FT-IR) were recorded in the range of 4000–400 cm^{-1} using KBr pellet technique on a FT-Raman Module (Nicolet, America) instrument. X-ray photoelectron spectroscopy (XPS) analysis was performed on an ESCALAB 250xi spectrometer (Thermon Scientific). Water contact angle (CA) measurement was performed on a CA meter (DSA100, Kruss).

Results and discussion

In this work, we used commercial nickel foam as an electrode for fabrication of PPy foam. Polypyrrole is a heterocyclic kind of conjugate polymer materials, which has been widely used in field of oil/water separation [45–47]. With the simple electrodepositing method, a new kind of three-dimensional (3D) PPy material based on the nickel foam was fabricated, as shown in Fig. 1a. SEM was performed to evaluate the morphology of PPy material. From Fig. 1b, the as-treated commercial nickel foam shows a macroporous structure with smooth surface morphology (Fig. 1b, inset). After coating with PPy particles, as seen in Fig. 1c, the PPy film on the nickel foam exhibits lotus-like

structure morphology with good roughness and highly porosity [48–50]. Higher magnification SEM image (Fig. 1c, inset) shows the PPy foam with thin films in diameter range of 4–5 μm, which is consisted of micrometer-sized PPy particles with average size of 8 μm.

The surface wettability was evaluated by CA measurement. With the hydrophilic reason of PPy in nature, the proposed PPy foam shows a superhydrophilic property with a water CA of ca. 0°. Obviously, the PPy foam can hardly be applied in the capture of organics and oils from water. To obtain superhydrophobic surfaces of PPy foam, the modification of hydrophobic low-surface-energy material with nano- or micro-sized roughness on the substrate is greatly essential [51–53]. Recently, many absorbents with superhydrophobicity and superoleophilicity, which were achieved by surface modification with low-surface-energy chemicals such as polytetrafluoroethylene [2], tetraethoxysilane [54], polydimethylsiloxane [55], etc., have been issued and successfully used in the capture of organics and oils from water. Choi et al. [6] reported an eco-friendly sugar-templated poly-dimethylsiloxane sponge promoted potential in environmental applications of oil/water selective separation. Also, Jiang and coworkers [2] studied the superhydrophobicity and superoleophilicity mesh film with a rough surface composed mainly of low-surface-energy PTFE used effectively for the separation of oil and water. Accordingly, to change the surface chemical composition, we treated the proposed PPy foam using a dip-coating technique that provided a low-surface-energy material such as FAS onto the whole surface of porous foam to alter its surface wettability, which resulted in its superhydrophobicity by combination with the microscopic roughness. FAS is a superhydrophobic and moderately superoleophilic material with low-surface energy. As anticipated, upon hydrophobic treatment of FAS, the proposed PPy foam successfully changed from superhydrophilicity to superhydrophobicity, as is made evident by its water CA of 155° (Fig. 2c). Importantly, the proposed FAS-treated PPy foam (FPF) has both properties of superhydrophobicity and superoleophilicity. To demonstrate these excellent properties, we measured the water CA to investigate the surface wettability of FPF. As shown in Fig. 2b, when two water droplets (dyed with methylene blue) were allowed to sit on the rough surface of FPF, the water droplets kept spherical and translucent, which was consistent with the water CA of FPF. In contrast to its high hydrophobic performance, the FPF exhibits good oleophilicity after coating of low-surface-energy material. For instance, when a benzene labeled with Red oil O was put on the surface of FPF upon the commercially white sponge, it was quickly absorbed into the block of FPF and transferred onto the
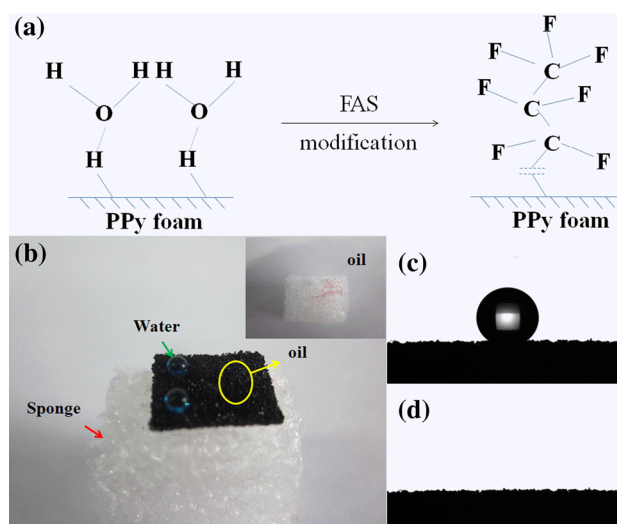

Fig. 2 a The process of PPy foam with FAS modification. b Snapshots of water and benzene droplets on the FPF. Inset is the sponge with absorbing benzene. c The water CA measurement of FPF, and d the oil CA measurement of FPF

porous surface of sponge (Fig. 2b, inset), resulting in the oil CA of ca. 0° (Fig. 2d). It should be due to that the chain of volatile silicone-contained polyfluorinated alkanes was contacted with the hydrogen atom of PPy and outstretched, taking place of the original hydrogen bond resulting from the effect of H_2O, as seen in Fig. 2a.

To investigate the effect of surface composition on the surface wettability of FPF, FT-IR spectra was performed. As shown in Fig. 3, the peaks appeared at 2934, 1634, and 1552 cm^{-1} were attributed to the results of the =C–H, C=C, and C–C stretching vibrations, respectively. The peak at 1400 cm^{-1} was assigned to the in-plane C–N stretching vibration [56]. Also, the peaks observed at 906 and 796 cm^{-1} mainly indicated the characteristic of in-plane C_β-H binding deformation and vibration of pyrrole, suggesting that the polymerization combination is attributed to the form of α–α combination between pyrrole rings [57, 58]. Compared with the pure PPy, however, such new peaks at 1240, 1200, and 1148 cm^{-1} were fully proved to demonstrate the bond of polyfluorinated alkanes (Fig. 3, inset), in good accordance with the literatures [6, 55].

Furthermore, we also use XPS to confirm the effect of FAS modifier on the wettability of PPy foam. From Fig. 4, the peaks appeared at 285.0, 408.02, and 863.70 eV are attributed to the C1s, N1s, and Ni2p, respectively [59, 60]. Obviously, these peaks mentioned above indicated the PPy film coated on the nickel foam. Specially, some characteristic peaks were observed at 689.20, 102.35, and 532.35 eV, which indicated the F1s, Si2p, and O1s and was in good agreement with the previous literatures [61, 62],
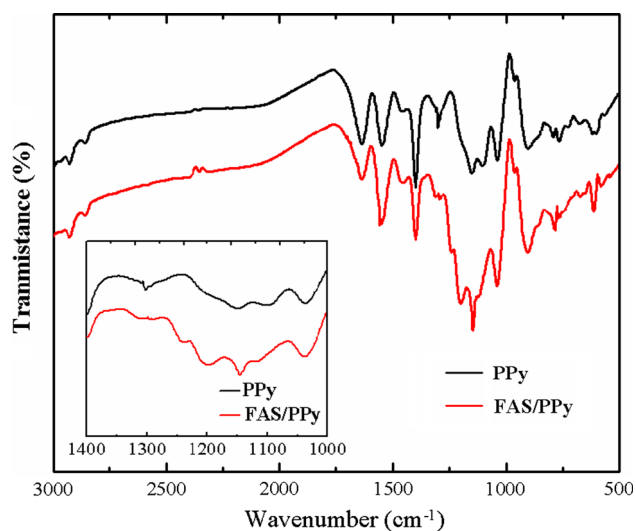
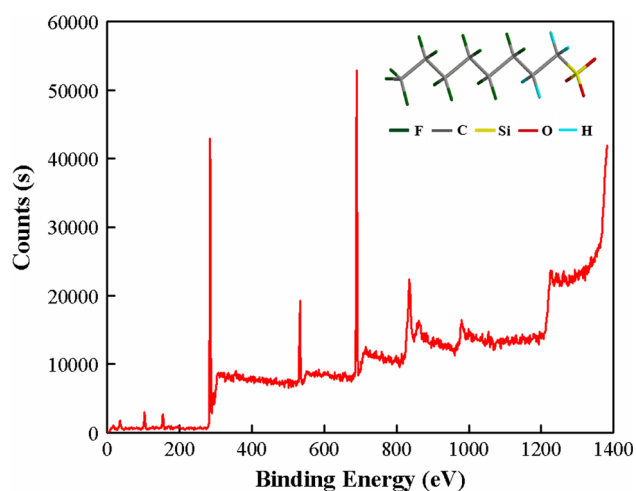Fig. 3 FT-IR spectra of PPy before and after FAS treatment

Fig. 4 XPS spectra of PPy after FAS treatment

corresponding to 22.83 at.% fluorine, 5.61 at.% silicon, and 5.92 at.% oxygen, respectively. It should be obviously explained that volatile polyfluorinated silicone-contained alkanes in the form of short FAS chains form a conformal layer on the surface of PPy foam and subsequently cross-link, to lead to the formation of a silicone coating, which is in accordance with the result of FT-IR [24].

Taking advantage of its superhydrophobicity and superoleophilicity as well as its porous feature, the FPF can be a promising candidate for capture of organic solvents and oils from water. As shown in Fig. 5a–c, when the FPF was contacted with a benzene droplet (dyed with Red oil O) on the water surface, it could be quickly absorbed by the FPF without absorbing any water, indicating its excellent selective absorption property. Also, we found that the capture of organics (in this case tetrachloromethane) could be conducted underwater by the FPF (Fig. 5d–f). The fast absorption of organic solvents used should be mainly attributed to the high oleophilic character of the FPF in combination with its porous feature.

Most interestingly, we found that the FPF could possibly be used as a selective membrane (seen in Fig. 6a) for both organic solvents and oils, with great potential for the removal of toxic organic contaminants and oil spills from water. As shown in Fig. 6b, when a mixture of benzene and red O oil was poured onto the surface of superoleophilic FPF, the dyed benzene solution can be quickly absorbed and freely pass through the FPF to achieve high efficiency, illustrating the strong oleophilic performance of FPF. However, the water droplets (dyed with methylene blue for easy observation) were steadily held on the FPF surface (Fig. 6c) and kept spherical (Fig. 6c, inset), implying that the special surface wettability enabled the modified PPy foam for the capture of organics and oils from water with a high absorption selectivity. Meanwhile, as seen in Fig. 6d, e, when the water droplet was squeezed or pulled between two small pieces of FPF, it could also keep spherical, representing the excellent stability of superhydrophobic property of FPF, and revealing this observation can make the FPF the promising candidate as a "mechanical hand" for transferring small quantity of aqueous samples for microsample analysis [59]. Furthermore, the absorption capacity is an important factor for many oleophilic absorbents. For traditional bulk absorbent materials, the absorption efficiency mainly depends on the interaction between the absorbents and the organics [63], and the absorbing capacity is limited. In contract, for the FPF as membrane, the absorption process was continual, which could have potential in the purification of organics separation or oil leakage in water. On the other hand, as a porous-membrane material, the absorption capacity mainly depended on the density of various organics, different from the traditional absorbent materials whose adsorption capacity is limited by their bulk volume. We believe such FPF would be used widely in oil spills cleanup especially for large areas oil leakage on sea or severely polluted water regions.

The recyclability and recoverability of superhydrophobic FPF for capture of organics and oils address key requirements in practical oil cleanup applications, which is an important factor for evaluation of their practical usage performance. In this case, the absorbed organics (in this case benzene) in the FPF can be removed simply by heat treatment or washing. As shown in Fig. 7, the water CA values of the FPF do not change greatly with an average value of 145° (Fig. 7), indicating good recyclability and recoverability due to the tight wrapping of FAS film onto the surface of PPy foam. On the basic
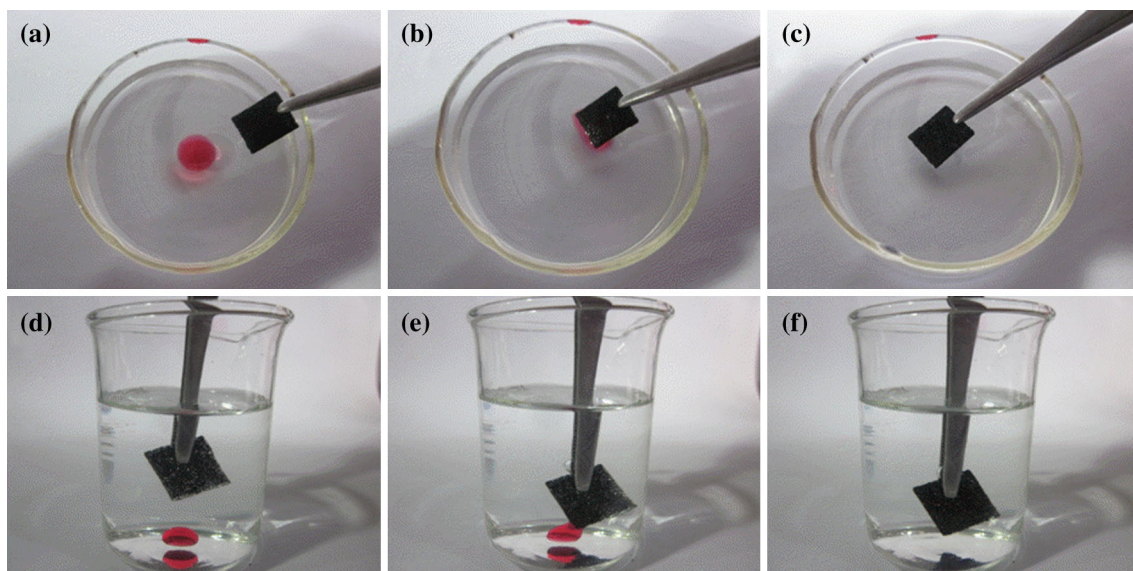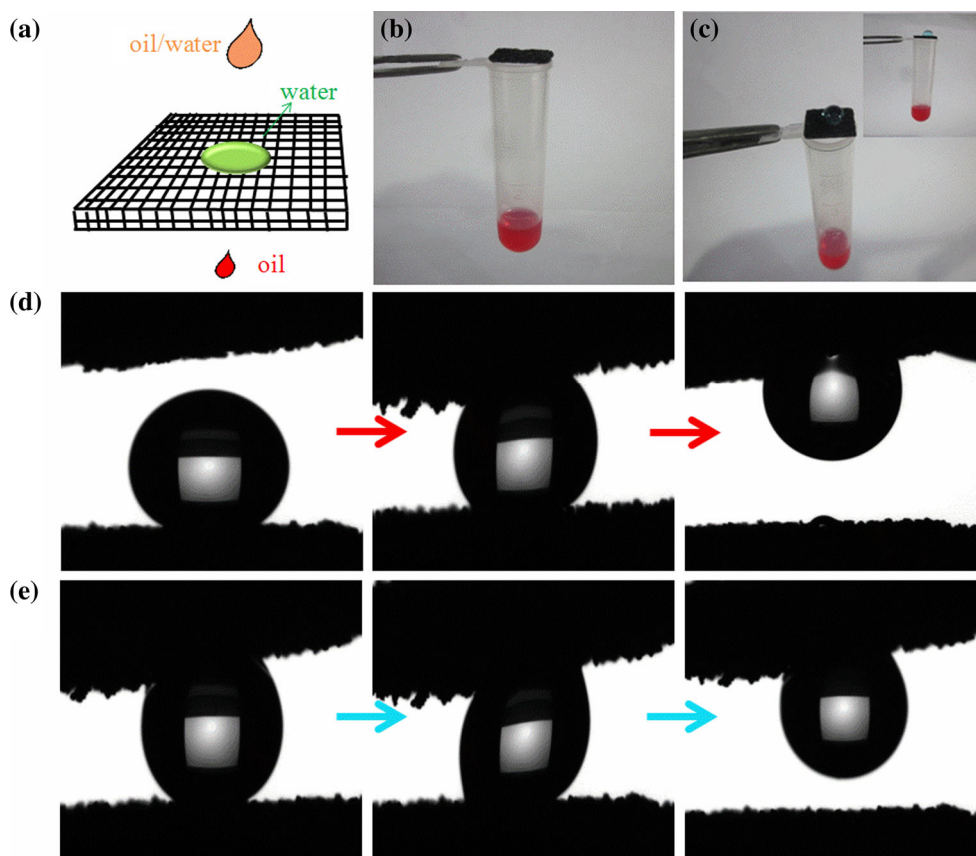
Fig. 5 Snapshots of FPF used for removal of benzene (**a–c**) and chloroform (**d–f**) from water

Fig. 6 a Diagram of separating membrane. The separating membrane for **b** oil and **c** water, *inset* is the front view of water droplet on the FPF surface. The squeezing (**d**) and pulling (**e**) states of water droplet between two pieces of FPF

point, the FPF would be a desirable material in that it can facilitate the recycling of oil-absorbent materials by allowing for the repeated capture and release of oils and organic solvents. Our study could provide a versatile method for creation of 3D absorbing materials by simple electrodeposition method. Furthermore, compared with those superoleophilic absorbents which were fabricated by complicated process or need multistep procedures, the fabrication of such polymer-coated foam using electrodeposition method and surface modification are simple
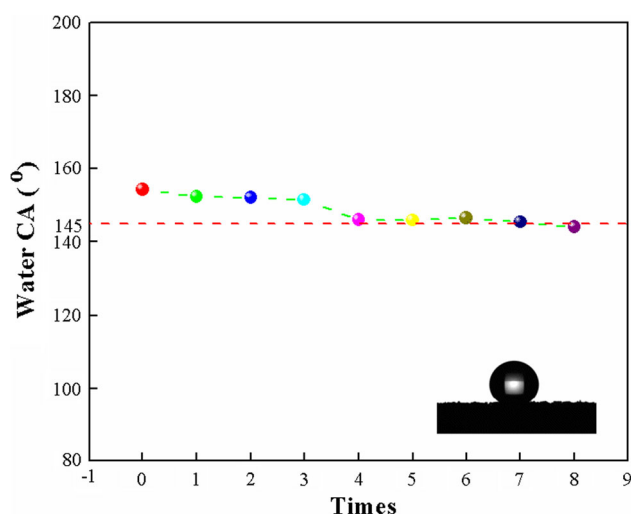
Fig. 7 Recyclability test of FPF. FAS-treated PPy foam repetitively absorbed benzene and released its vapor under heat treatment (80 °C) for 9 times

and easy to be scaled up for large-scale practical applications.

Conclusion

In summary, three-dimensional superhydrophobic material was fabricated by coating of conductive polymers such as PPy onto commercial nickel foam by the electrodepositing method. The superhydrophobic and superoleophilic properties of FPF should be contributed to the formation of nanostructured surface roughness of polymers on the surface of nickel foam by combination with low-surface-energy materials modification. The FPF could be well used as a membrane with high selectivity for the capture of oils and organic solvents from water, which would have great potential in fields of removal of oils and organics from water and is of technological significance.

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