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Oil–Water Separation by ZnO-Based Superhydrophobic PU Sponges

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Continuous oil–water separation is not only an important topic for scientific research but also for practical applications to clean oil from industrial oily wastewater and oil-spill pollution. In this work, polyurethane sponges are coated by ZnO using dip coating technique. ZnO-coated sponges are modified by stearic acid to achieve superhydrophobicity. The ZnO-coated sponges exhibit water contact angle ≈165° and oil contact angle ≈0°. The prepared superhydrophobic sponge is sustained in oil–water separation and in separation of oil–hot water mixture. Also the wetting properties of the sponge are stable in mechanical test like cutting and twisting. Stearic acid modified ZnO-coated sponge holds good promise for oil-spill cleanup as well as oil/water separation from harsh environments.

1. Introduction

Cleaning of industrial oily wastewater and oil spills in a marine environment as well as polluted oceanic water is a worldwide challenging task.[1–3] Various traditional methods are used such as mechanical collection, oil, skimming, and controllable burning to cleanup oil. These methods are expensive and show low-efficiency and environmental incompatibility.[4] The special wettability and self-cleaning property of natural lotus leaf and various insects inspired the researchers to develop superhydrophobic surfaces having water contact angle greater than 150° and roll off angle less than 10°.[5,6] The hierarchical superhydrophobic surface can be easily developed on glass or other substrates such as foam, paper, sponge/mesh, metal, and wood by optimizing the surface roughness and surface energy.[7–11]

For the first time, Feng et al.[12] have used the superhydrophobic and superoleophilic coated mesh for oil–water separation application. Subsequently, the superhydrophobic and superhydrophilic materials have been used to apply on sponges, which absorbs oil and strongly repel the water.[13] The superhydrophobic-superoleophilic sponge/mesh exhibited efficient and fast oil–water separation capability, good repeatability, and reusability, robust mechanical, chemical, and thermal stability.[14] The silica based superhydrophobic aerogels were also used for efficient oil–water separation.[15] Our research group[16] have fabricated crater-like superhydrophobic leaf mesh by simple deposition of SiO_2-PS nanocomposite on leaf mesh which exhibited efficient oil–water separation. Also we have fabricated a free-standing sawdust–polystyrene (SD–PS) composite based superhydrophobic pellet

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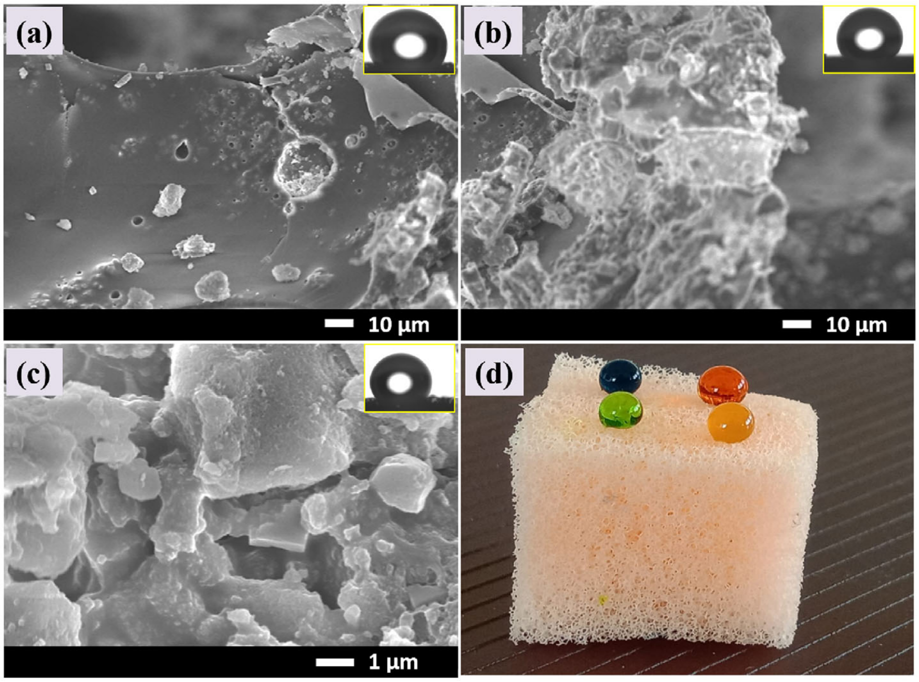

Figure 1. Scanning electron microscopy images of a) S1, b) S2 and c) S3 samples. d) The optical photograph of color water drops placed on S3 sample.

which showed could separate oil from oil–water mixture, oil–muddy water mixture, and oil–hot water mixture.[17] Zhu et al.[18] have coated polysiloxane layer onto the surface of 3D porous PU sponges through a one-step solution immersion method. This sponge showed highest reusability and durability among the reported absorptive materials. Tran[19] has prepared superhydrophobic and magnetic PU sponge modified with ZnO, stearic acid (SA) and Fe_3O_4 to provide the necessary high roughness, low surface energy and magnetic responsiveness, respectively. Li et al.[20] have reported the modification of PU sponge with ZnO microrods and palmitic acid (PA) which showed excellent absorption of oil over water, and high reusability. The micro-ZnO microrods increased the surface roughness of PU sponge, which eventually helped to improve the hydrophobic and oleophilic properties and the modification by palmitic acid (PA) reduced the surface energy of ZnO-PA sponge and makes the PU sponges superhydrophobic in nature with excellent selectivity for oil. Xiang et al.[21] have prepared ZnO-stearic acid (STA) based superhydrophobic nanocoating on sponge which absorbs oil (1,2-dichloroethane) from oil–water mixture. Cheng et al.[22] have fabricated excellent anti-wetting, high absorption capacity, durable ZnO based robust superhydrophobic PU sponge for oil water separation. We have also reported the preparation of superhydrophobic melamine sponge using hydrophobic silica nanoparticles which revealed oil uptake/absorption capacity of 27 times of its own weight.[23]

Herein, a durable superhydrophobic ZnO-coated sponge was prepared by simple immersion and subsequent drying process. The as prepared ZnO sponge was modified by stearic acid to achieve the superhydrophobic wettability. The prepared superhydrophobic sponge showed excellent oil absorption ability and reusability. The wetting stability of superhydrophobic sponge was investigated by adhesive tape test.

2. Result and Discussion

2.1. Surface Morphology and Wettability of Modified Sponges

The surface morphology of the SA modified ZnO coated sponges were investigated by SEM micrograph. From SEM micrograph (**Figure 1**), it is clearly seen that the roughness changes with amount of zinc acetate dehydrate used in the preparation of the coating solution. The samples S1 and S2 reveals nearly smooth surface. However, sample S3 exhibits porous structure with hierarchical roughness which can trap air pockets and hence can show superhydrophobic wettability. The wettability of the sponges was analyzed by measuring contact angle of water and oil. All modified sponges showed superoleophilic nature with oil contact angle nearly 0°. The water contact angle varied with amount of zinc acetate dehydrate in coating solution. The low concentration of zinc acetate dehydrate forms negligible amount of ZnO particles and hence the surface is smooth in nature. The samples S1 and S2 revealed WCAs of nearly 155° and 160°, respectively and hence superhydrophobic nature. However, water contact angle increased to 165° in case of S3 samples due to trapped air pockets in the hierarchical structure. The water drops exhibit spherical shape when placed on the S3 sample (Figure 1d) and roll off quickly at small tilting.

2.2. Oil–Water Separation

The oil–water separation can be carried out in two ways such as by superhydrophobic sponge and mesh. The oil–water separation by superhydrophobic mesh have disadvantages, when separating oil spills from sea water. Here, we used a peristaltic pump for continuous oil–water separation. The practical arrangement of continuous oil–water separation is shown in **Figure 2**. Various

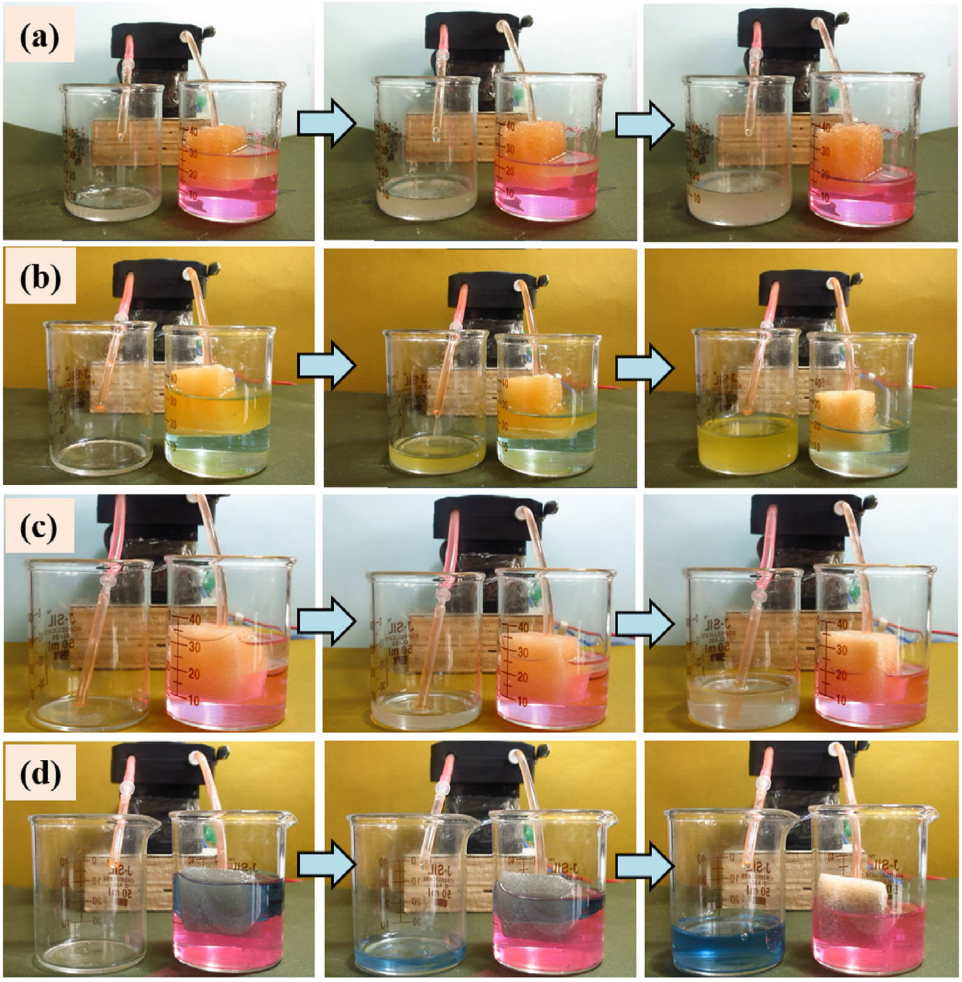

Figure 2. Continuous oil collection using a peristaltic pump a) diesel, b) petrol, c) coconut, and d) kerosene from oil–water mixture.

oils such as petrol, disel, kerosene, and coconut oil were used for invistigation of oil–water separation. The oil–water mixture were prepared by adding 10 mL oil in 15 mL water. The S3 sample was fixed at the end of inlet pipe and immersed in the mixture. The sample absorbed oil quickly when it came in contact with mixture and absorbed oil was removed by pump. In only few seconds, oil was completely removed by superhydrophobic sponge. The process of removal of diesel, petrol, coconut, and kerosene from oil–water mixture is shown in Figure 2a–d, respectively.

2.3. Durability of the Superhydrophobic Sponge

The durability of the superhydrophobic sponge was checked by physical methods including compressing, twisting and cutting.[24] A water drop revealed spherical shape on S3 sample, whereas an oil quickly got absorbed inside the sample as shown in **Figure 3**a. The S3 sample was compressed and twisted many times and observed its effect on the wetting property. A water drop shows similar shape and contact angle after test, confirming good wetting stability. The compressed and twisted S3 sample is shown in Figure 3b. The S3 sample was cut in middle part (Figure 3c), the cross sectional sponge surface showed similar antiwetting property as superhyrophobic sponge. In Figure 3d, the water drop reveals spherical shape on cross section.

Additionally, we have checked the oil–water separation ability of S3 sample from the mixture of hot water and diesel. Li et al[25] have also utilized the attapulgite coated superhydrophobic polyurethane sponge to efficiently separate oil from hot water. The same research group[26] have used superhydrophobic candle soot and silica composite sponges to easily separate out an oil from the hot water having temperature of nearly 92 °C. The 40 mL water filled glass beaker was kept on hot plate with temperature controlled at 80 °C and 10 mL diesel was added in it. The diesel was quickly picked up by the S3 sample from hot water. The oil removal process is shown in **Figure 4**. The oil absorbed sponge was taken out and collected oil by squeezing (Figure 4d).

3. Conclusion

A superhydrophobic and superoleophilic ZnO-coated sponge was prepared using facile immersion and drying technique. The modified PU sponge revealed the water contact angle of 165° along with oil contact angle of 0°. The prepared sponge

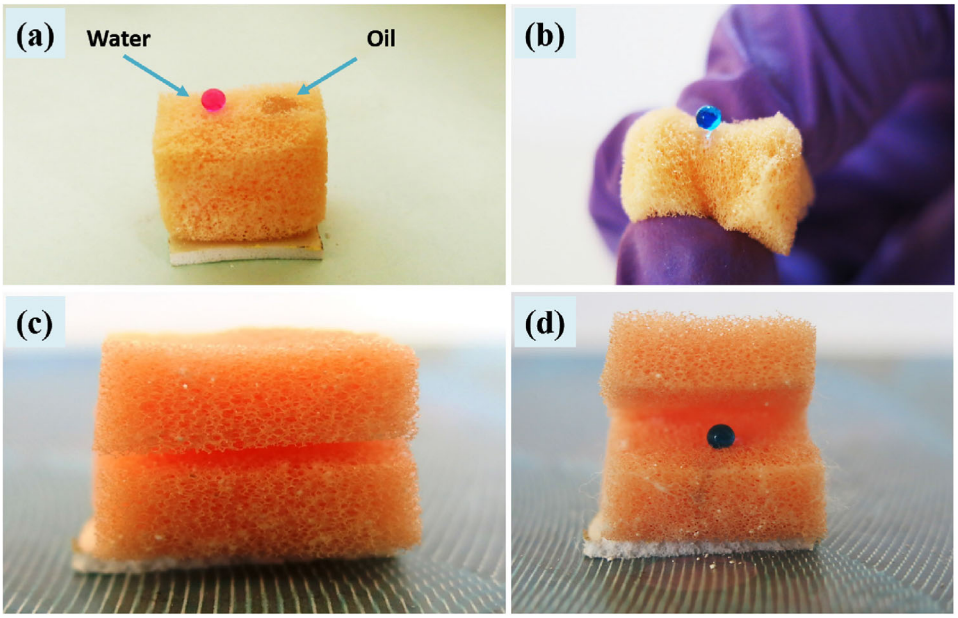

Figure 3. a) Optical image of water and oil drop on S3 sample, b) twisting of S3 sample and c–d) S3 sample cut in middle part and checked its wettability.

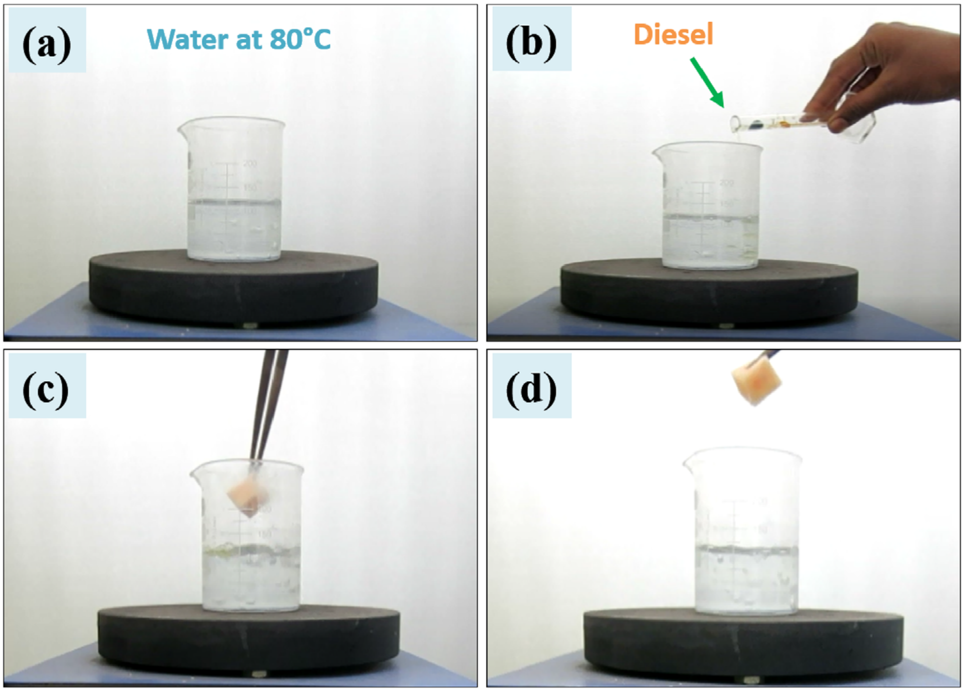

Figure 4. The oil–water separation by S3 sample from oil–hot water mixture.

showed good superhydrophobicity after many time compressing, twisting, and cutting test. The prepared sponge exhibited excellent ability to continuously remove all types of oil including diesel, petrol, coconut oil and kerosene from oil–water mixture. Also exhibited good stability in separation of oil (diesel) from hot water. So this superhydrophobic sponge is a good candidate for the oil cleanup from industrial wastewater and oil spills.

4. Experimental Section

Materials: Zinc acetate dihyrate was purchased from Spectrochem PVT. LTD, India. Stearic acid (SA) was procured from Sigma Aldrich, USA. Iso-propyl alcohol was bought from Molychem PVT. LTD, India. Diethanolamine was purchased from Thomas Baker PVT. LTD, India. Polyurethane sponge was obtained from local market, Jath, India.

Preparation of ZnO Coated Sponge: The polyurethane (PU) sponges were cut into cubes (2 cm × 2 cm × 2 cm) and washed ultrasonically in acetone and distilled water to remove possible impurities. The washed sponges were squeezed well and dried at 50°C for 30 min. A coating solution was prepared as reported in literature.[27] At first, 1 g zinc acetate dehydrate was dissolved in 50 mL iso-propyl alcohol using magnetic stirrer at room temperature. After 1 h stirring, 250 μL diethanolamine (DEA) were added drop wise and stirring was further continued at temperature ≈60 °C for 1 h with speed ≈250 rpm. The prepared solution was kept overnight to complete hydrolysis and condensation processes. In this process, DEA act as a complexing agent to form metal oxide. The pre-cleaned sponges were dipped inside the prepared coating solution for 1 min. Then, sponge was squeezed well and dried at 100 °C for 30 min to remove solvent. In this way, five depositions were taken on the sponge. Three different coating solutions with zinc acetate dehydrate concentration of 1, 2 and 3 g were used to coat the sponge and named as S1, S2, and S3 samples, respectively.

Modification of ZnO Coated PU Sponge by Stearic Acid: The stearic acid solution was prepared by adding 1.25 g SA in 50 mL ethanol. A mixture was stirred at 200 rpm using magnetic stirrer to dissolve SA completely. The ZnO coated sponge was dipped in stearic acid solution for 30 min. This sponge was squeezed and dried at 80 °C for 30 min.

Characterizations: The morphology of modified sponges was observed by using scanning electron microscope (SEM, JEOL, JSM-7610F, Japan). The water contact angle and oil contact angle measurement were carried out using contact angle meter (HO-IAD-CAM-01, Holmarc Opto-Mechatronics Pvt. Ltd. India). The oil–water separation ability of modified sponges was tested using kerosene, petrol, diesel, and coconut oil. The anti-wetting property of modified sponges was checked by cutting and twisting.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

contact angle, superhydrophobic, wettability and lotus leaf, ZnO

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