



Superhydrophobic PU Sponge Modified by Hydrophobic Silica NPs—Polystyrene Nanocomposite for Oil–Water Separation

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In this study, the hydrophobic silica nanoparticles (NPs) are synthesized by simple sol–gel processing of polymethylhydrosiloxane (PMHS). The nanocomposite solution is prepared by adding hydrophobic silica NPs in polystyrene solution and applied on the skeleton of polyurethane sponge by simple immersion-drying process. The as-prepared sponges exhibited superhydrophobic property with water contact angle 161° and oil contact angle nearly 0° and can separate oil from oil–water and oil–muddy water mixture. The superhydrophobic sponge has sustainable anti-wetting property under cross sectional cutting, pressing and twisting, and different pH environment. Such superhydrophobic sponge is suitable for practical application on a large scale.

1. Introduction

A spillage of oils in ocean and river results in a serious harm to the environment. In the last century, oily waste water treatment technologies such as air flotation,^[1] burning,^[2] gravity separation,^[3] membranes separation^[4,5] faced great challenges, such as secondary environmental pollution, low efficiency, time consuming, and high cost. A new technology in materials science has been developed for easy oil–water separation using superhydrophobic nanomaterials. Like lotus leaf, on superhydrophobic surface, the water drop reveals the contact angle greater than 150°

and roll off the surface quickly by little tilting. The hierarchical superhydrophobic surfaces can be developed by applying thin layer of low surface energy materials.^[6–9] The hydrophobicity of the rough surfaces can be increased after modification with low surface energy materials.^[10–13]

Recently, such superhydrophobic materials applied on mesh and sponges with special wettability are being utilized for efficient oil water separation process. The superhydrophobic and superoleophilic characteristic of the material was illustrated to be used for oil water separation in many studies.^[14–20] The superhydrophobic-superoleophilic sponge/mesh exhibited high selectivity toward various oils and organic pollutants, efficient, and fast oil–water separation capability, good repeatability, and reusability, robust mechanical, chemical, and thermal stability.^[21] Due to extreme water repellent and quick oil absorbance property, this special wetting superhydrophobic material shows the high separation efficiency and stability. However, complex preparation process and high costs materials are restricting their industrial applications.^[22,23] Sponge is one of the low-cost 3D porous material with larger surface area and used as an ideal substrate for oil water separation. Latthe et al.^[24] have fabricated crater-like superhydrophobic leaf mesh for oil water separation by depositing nanocomposite of SiO_2 and polystyrene (SiO_2 -PS) on a naturally dried *Tectona Grandis* leaf mesh. Recently, we have developed a facile strategy to prepare a free-standing superhydrophobic pellet using sawdust-polystyrene (SD-PS) composite, which exhibited higher than 90% of oil–water separation efficiency.^[25] Wang et al.^[26] have applied hierarchical

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DOI: 10.1002/masy.202000035

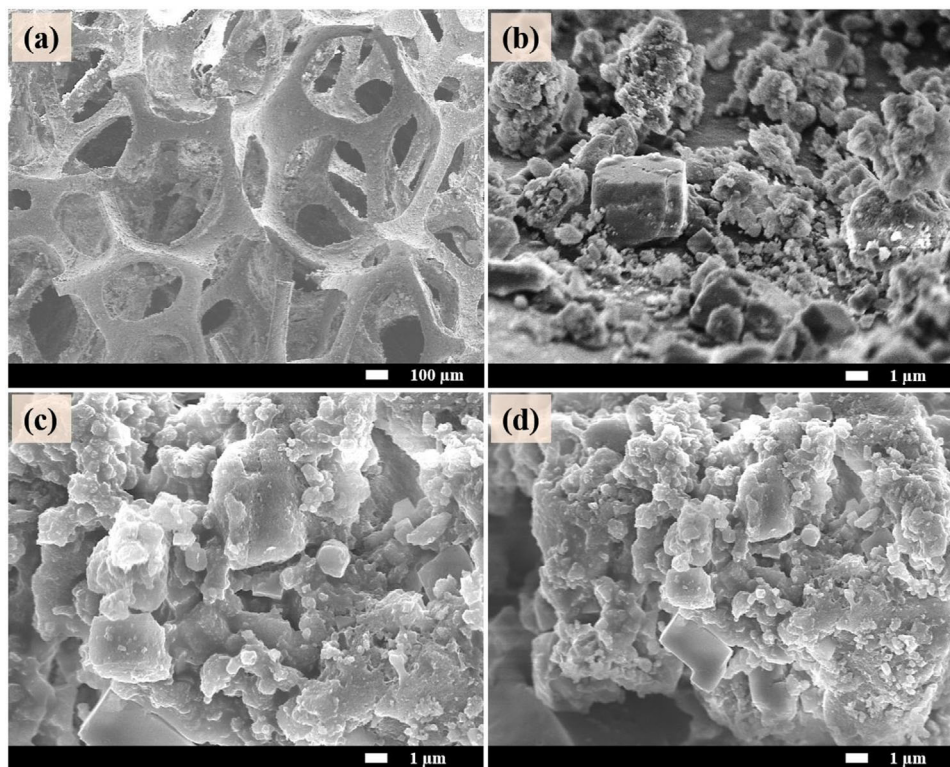


Figure 1. SEM images of a) pristine PU sponge, b) P1, c) P2, d) P3 sample.

micro-nanostructured coating of polydopamine on melamine sponge by simple self-polymerization process, and finally, the sponge was modified by dodecanethiol to achieve superhydrophobic and superoleophilic wetting properties. The prepared sponges could easily separate oil layer from water as well as oil–water emulsion. The superhydrophobic sponges quickly absorbed various oils up to 20 times of its own weight. Xie et al.^[27] have prepared superhydrophobic melamine sponges by modifying with polydopamine and hydrophobic silica NPs. These superhydrophobic sponges exhibited good mechanical durability, high adsorption capacity, and excellent recyclability for more than 80 times. Moreover, the superhydrophobic sponges could continuously separate oil from salty water with ease. Gao et al.^[28] have used two-step strategy like silica NPs adsorption and silanization covering on melamine sponge to achieve water-repellent properties. The sponges were durable against ultrasonication and corrosive environments and could effectively separate range of oils from water. Zhang et al.^[29] have loaded hydrophobic thiolated graphene on polyurethane (PU) sponge by simple dipping-drying process and these superhydrophobic sponges revealed high selectivity and recyclability. Cao et al.^[30] have used new carbon-based material such as nanodiamonds to fabricate superhydrophobic sponges. The PU sponge was coated by hydroxylated nanodiamonds with polydopamine and subsequent surface modification using 1H,1H,2H,2H-perfluorodecanethiol. These superhydrophobic sponges showed excellent oil–water separation property with high organic adsorption capacity. Li et al.^[31] have simply modified the PU sponge by applying superhydrophobic attapulgite (APT) on the skeleton of the sponge. The prepared

superhydrophobic sponges could separate oil from mixtures and various corrosive solutions and hot water. Beshkar et al.^[32] have modified the PU sponge by simply immersing in the suspension of straw soot and magnetic NPs. The as-prepared sponges revealed superhydrophobicity and could separate various organic solvents from water with 30 times recyclability. Merely superhydrophobic silica NPs coated melamine sponge revealed oil uptake/absorption capacity of 27 times of its own weight.^[33]

In this study, we have synthesized the hydrophobic silica NPs by simple sol-gel processing of polymethylhydrosiloxane (PMHS). The nanocomposite solution was prepared by adding hydrophobic silica NPs in PS solution and applied on PU sponge by simple immersion-drying process. The as-prepared sponges exhibited superhydrophobic property and could separate oil from oil–water and oil–muddy water mixture.

2. Results and Discussion

2.1. Surface Morphology and Wettability of the Sponges

The microstructure of pristine PU sponge exhibits 3D interconnected micropores with diameter in the range of 150–500 μm (Figure 1a).^[34] As the concentration of silica NPs in the nanocomposite is very less in P1 sample, the separate aggregates of silica NPs having sizes in the range of 1–10 μm were observed (Figure 1b). However, the interconnected aggregates of silica NPs were observed for P2 and P3 sample (Figure 1c,d) due to higher concentration of silica NPs in nanocomposite structure. The silica NPs were bound together by PS. The P2 and P3 samples

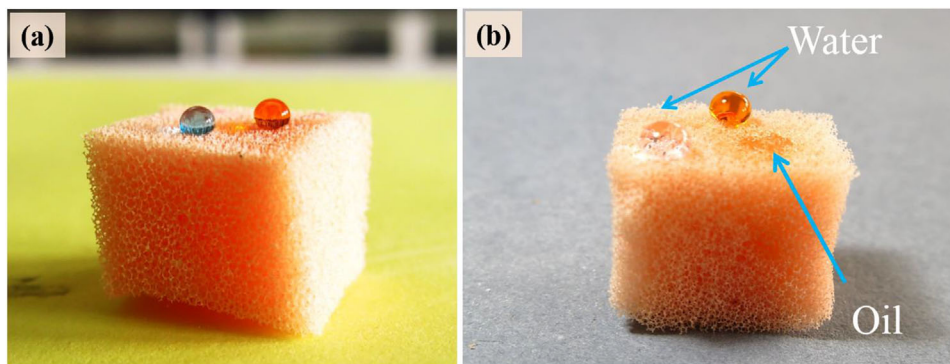


Figure 2. Optical images of a) water drops on P3 sample and b) water and oil (petrol) drops on P3 sample.

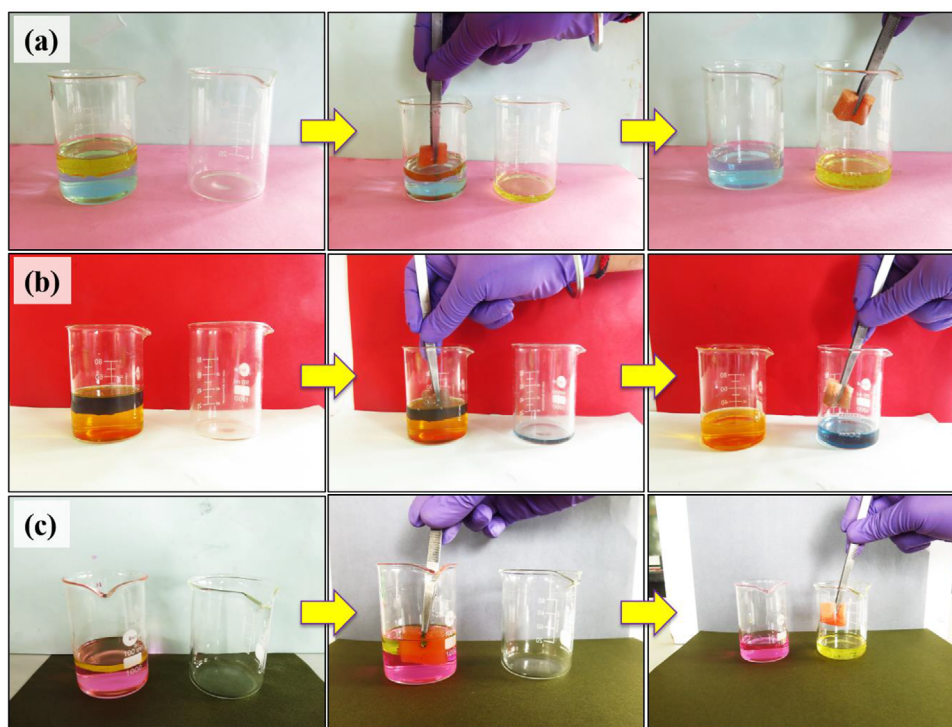


Figure 3. Optical images of process of removal and collection of a) diesel, b) kerosene and c) petrol from oil–water mixture by P3 sample.

reveal rough surface morphology, which is useful to achieve superhydrophobic wettability in the sponges. For all the samples, the silica NPs–PS nanocomposite was heavily deposited in the skeleton of sponge.

The wettability of the modified sponges also depends upon the concentration of silica NPs in the nanocomposite. The P1, P2, and P3 samples exhibited the water contact angle of 143°, 150°, and 161°, respectively. Due to inhomogeneous coverage of nanocomposite structure on sponge, P1 sample shows less water contact angle, whereas the nanocomposite material uniformly and heavily got deposited on P2 and P3 samples resulting in water contact angle in superhydrophobic state. All the samples exhibited superoleophilic property. **Figure 2** shows the optical photograph of water drops and oil (petrol) drops on P3 sample. Water drops hardly stay on the sample, whereas an oil drop placed on

the sample was quickly absorbed inside the sponge with contact angle $\sim 0^\circ$ confirming its superoleophilic characteristic. Hence, P3 samples can be further used for efficient oil–water separation application.

2.2. Oil–water Separation Ability of Superhydrophobic Sponge

The absorption separation process of oil from oil–water mixture by superhydrophobic modified sponge is shown in **Figure 3**. The oil–water mixture was prepared by adding 10 mL oil in 10 mL water. Three types of oils such as diesel, kerosene, and petrol were used to study the oil–water separation. The superhydrophobic sponge was dipped in oil–water mixture and it was observed that superhydrophobic sponge quickly absorbed oil in few seconds. The oil–absorbed sponge was pulled up and squeezed in

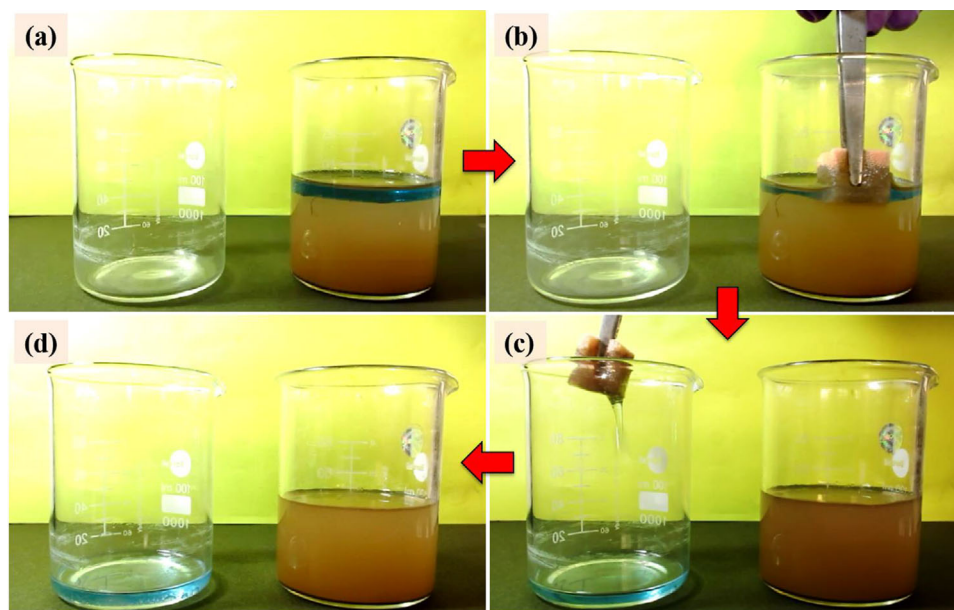


Figure 4. Optical images of removal and collection of oil from the mixture of oil–muddy water by P3 sample.

another beaker to collect oil. Figure 3 depicts optical images of absorption and squeezing process of sponge. The oil–water separation ability of superhydrophobic sponge was tested by using diesel (Figure 3a), kerosene (Figure 3b), and petrol (Figure 3c). So, this promising, facile, and energy-saving method can be used to remove the oil from oil-contaminated area.

In another way, the oil removal ability of sponge was tested using mixture of oil and muddy water. The muddy water was prepared by adding 10 g soil in 50 mL water by stirring. Five milliliter kerosene was added in muddy water and stirred well to mix oil in it. After few seconds, a layer of oil surfaced on muddy water. The oil was removed from muddy water by simply dipping superhydrophobic sponge in the oil–muddy water mixture (Figure 4). The porous structure of superhydrophobic sponge was able to absorb oil and repel muddy water completely.

2.3. Durability of Anti-wetting Property of Superhydrophobic Sponge

Several methods were adopted to investigate durability of anti-wetting property of superhydrophobic sponge such as adhesive tape and sandpaper abrasion test.^[35] As shown in Figure 5, the adhesive tape (Cellotape No. 405 having adhesiveness of 3.93 N/10 mm) was placed on P3 sample and a metal disc of 200 g was rolled on it to make good contact between the sponge surface and tape (Figure 5a,b). The tape was peeled off the sponge (Figure 5c). After tape peeling test, sponge displayed superhydrophobic property with water contact angle 160° as shown in Figure 5d. The sponge has lost superhydrophobic property in 12 cycles of adhesive tape peeling test due to removal of nanocomposite from the surface of sponge.

The abrasion resistance test was carried out using sandpaper (Grit No. 320). The superhydrophobic P3 sample was placed on sandpaper with load of 100 g and dragged with linear speed for

length of nearly 10 cm. This procedure is considered as one abrasion cycle and no contact angle change was observed on P3 sample. The sandpaper abrasion process is shown in Figure 6a–d. After 10 cycles, the WCA on P3 sample reached to 140° due to excessive damage to the surface by sandpaper. So, it was confirmed that the superhydrophobic sponge endures its wettability under adhesive tape and sandpaper abrasion test.

The wettability of superhydrophobic sponge was tested by taking cross-section cut and twisting. The superhydrophobic sponge was cut into three different cross-sectional positions, which look like stairs (Figure 7a). At every cross-sectional face of sponge, its original surface superhydrophobicity was sustained, which showed similar contact angle as on initial surface of superhydrophobic sponge. The water drops on cross-section of sponge are shown in Figure 7a. The superhydrophobic sponge pressed and twisted (Figure 7b) and observed its wetting state. A water drop acquired spherical shape on affected area of sponge under twisting and pressing. Hence, the P3 sample sustained superhydrophobicity under mechanical insults.

The chemical durability of superhydrophobic sponge was examined by different pH liquids. Acid and base liquid drops (pH~3 and pH~11) placed on P3 sample exhibited spherical shape (Figure 7c). Thus, superhydrophobic sponge can successfully withstand in various chemical environment. When superhydrophobic sponge was immersed in water, the mirror-like surface was observed (Figure 7d). The bright surface was due to the total reflection of light from air layer present on the surface of superhydrophobic sponge. The continuous air layer indicates the Cassie–Baxter nonwetting behavior.^[36,37]

3. Conclusion

A PU sponge was modified successfully by facile method using hydrophobic silica NPs and PS nanocomposite. The concentration of silica NPs in nanocomposite affects the

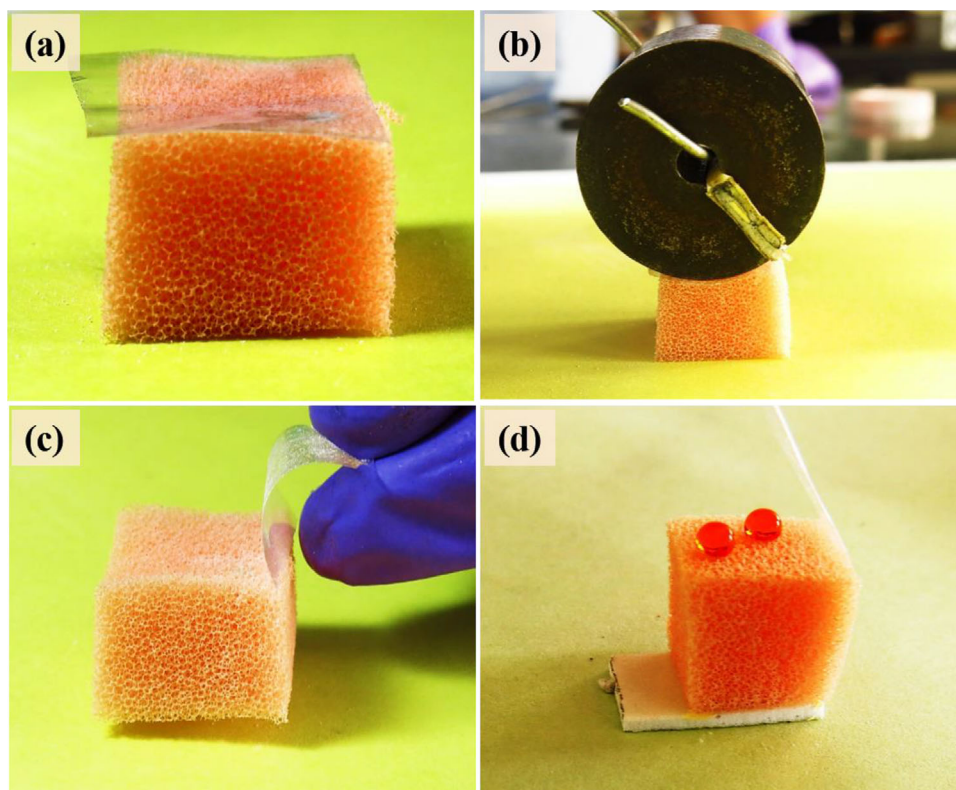


Figure 5. Optical images of a) placing adhesive tape on the sample, b) 200 g metallic disc rolling on tape, c) peeling off the tape, and d) color water drop on P3 sample.

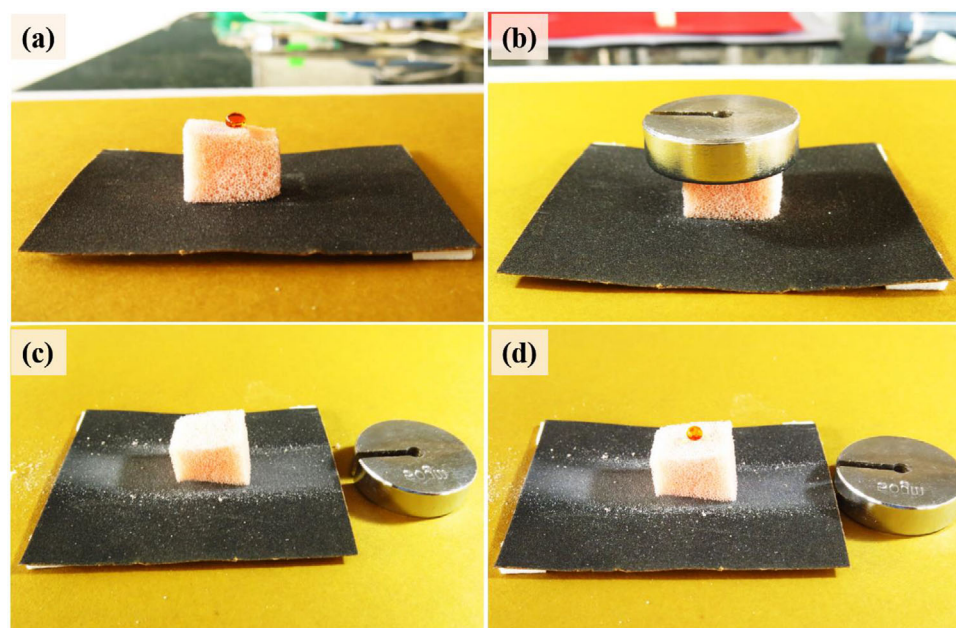


Figure 6. Optical images of a) P3 sample placed on sandpaper, b) 100g load applied on P3 sample, c) abraded surface of P3 sample, and d) color water drop kept on abraded surface of P3 sample.

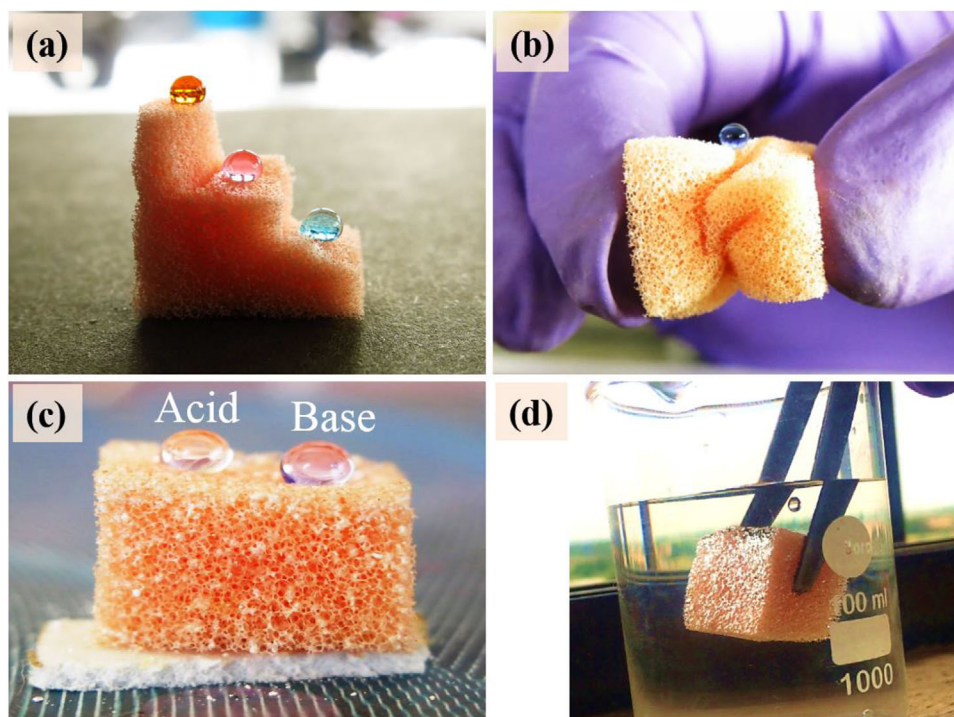


Figure 7. Optical images of a) water drops on cross section of P3 sample, b) twisted sponge with color water drop on it, c) acid and base drop on P3 sample, and d) mirror like surface displayed when P3 sample immersed in water.

wettability of the PU sponge. At optimum concentration of silica NPs in nanocomposite, the PU sponge exhibited WCA $\sim 161^\circ$ with superoleophilic (OCA $\sim 0^\circ$) property. The oil–water separation ability was tested by three different oils, including kerosene, petrol, and diesel. The superhydrophobic sponge revealed good oil–water separation ability in all type of oil–water mixture and also good removal of oil from oil–muddy water mixture. The mechanical and chemical durability of superhydrophobic PU sponge was tested under cutting in cross-section, pressing and twisting, adhesive tape and sandpaper abrasion tests, and under different pH liquids. The prepared superhydrophobic sponge can be availed for large-scale oil/water separation.

4. Experimental Section

Materials: Poly(methylhydrosiloxane) (PMHS, Average Mn ~ 1700 – 3200) and PS (PS, average Mw $\sim 192\,000$) were purchased from Sigma Aldrich, USA. Ethanol (99.9% AR grade), chloroform (AR grade), and sodium hydroxide pellets (AR grade) were purchased from Thomas Baker, PVT. LTD. India. PU sponge was bought from local market, Jath, India.

Sol–Gel Processing of PMHS: At first, 4.8 g PMHS was dissolved in 70 mL ethanol while stirring. A 0.08 g sodium hydroxide was dissolved in 2 mL distilled water and mixed in PMHS solution under constant stirring for 4 h at room temperature. The sol was completely transformed into gel after 4 h. The gel was dried at 80°C for 5 h. The obtained powder was washed several times using ethanol and dried at room temperature for 24 h followed by grinding into a fine powder using mortar and pestle. The obtained hydrophobic silica NPs were used to prepare the nanocomposite.

Preparation of Superhydrophobic Sponge: The PU sponges were washed repeatedly in ethanol and water for several times and dried at

80°C . The different nanocomposite solutions were prepared by dissolving 100 mg PS in 40 mL chloroform under constant stirring and added the 80, 120, and 180 mg of hydrophobic silica NPs in PS solution separately under constant stirring. A PU sponge was immersed in the nanocomposite solution for 5 min and dried at 100°C for 20 min and this procedure was repeated for 10 times. The sponges prepared with 80, 120, and 180 mg of hydrophobic silica NPs concentration in nanocomposites were labeled as P1, P2, and P3 samples, respectively.

Characterizations: The microstructure of the sponge was studied by scanning electron microscope (SEM, JEOL, JSM-7610F, Japan). The water and oil contact angles were measured using contact angle meter (HO-IAD-CAM-01, Holmarc Opto-Mechatronics Pvt. Ltd. India). To confirm the durability of the sponges, twisting, adhesive tape, and sandpaper abrasion test were carried out. The oil–water separation ability of the sponges was analyzed by separating oil from oil–water mixture.

Acknowledgements

This work is financially supported by DST – INSPIRE Faculty Scheme, Department of Science and Technology (DST), Govt. of India. [DST/INSPIRE/04/2015/000281]. SSL acknowledges financial assistance from the Henan University, Kaifeng, P. R. China. The authors greatly appreciate the support of the National Natural Science Foundation of China (21950410531).

Conflict of Interest

The authors declare no conflict of interest.

Keywords

modified sponge and oil–water separation, nanocomposite, superhydrophobic

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