# Oil-Water Separation: A Gift from the Desert

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Oil–water separation is the subject of theoretical and practical research around the world because of the frequency with which oil spills occur and the increasing amounts of oily industrial wastewater that are produced.[1–7] For example, the Gulf of Mexico oil spill in 2010 resulted in $780 \times 10^6$ L of oil being released into the sea.[8] This accident caused huge economic losses and had serious effects on the environment. Most animals and plants living in the sea near the incident died. Toxic compounds in the oil that were released, such as methylbenzene and hydrogen sulfide, quickly entered the food chain, and caused long-term harm to a wide array of biota, from algae to mammals. It is not possible to completely prevent this kind of environmental disaster from occurring again because the global demand for energy is growing. However, no effective solutions to minimize the occurrence of such events have yet been developed. Materials with super-wetting properties for water or oil (e.g., materials with superhydrophobic–superoleophilic or superhydrophilic–superoleophobic surfaces) have recently attracted increasing attention for use in oil–water separation applications because of the different interface effects of water and oil.[1,2] Superhydrophobic–superoleophilic mesh films were the first such materials to be used.[9–11] However, such "oil-removing" materials easily become blocked by the oil that adheres to the mesh as it passes through. This decreases the separation efficiency achieved and the service life of the materials.[12–14] Furthermore, such mesh films are not suitable for the gravity-driven removal of light oils (which are less dense than water) from mixed solutions because the water settles below the oil, creating a layer of water between the oil and the mesh film. The water layer prevents the oil from maintaining contact with the mesh film. Unfortunately, most oils are lighter than water. "Water-removing" superhydrophilic and superoleophobic materials have been developed to address the problems described above, and they have proved extremely effective in practical applications.[15–25] However, it is harder to produce a superoleophobic material (with an oil contact angle (OCA) greater than 150°) than to produce a superhydrophobic material because the surface tensions of oils are lower than the surface tension of water.[26–30] A surface that is superoleophobic in air will generally need to have a very rough micro/nanoscale hierarchical structure or a re-entrant surface curvature, and will need to undergo rigorous chemical modifications to give it a low surface free energy. An alternative method of preparing a superoleophobic interface in an aqueous medium, inspired by fish scales, was recently described by Jiang and co-workers.[31] They found that water trapped in the rough-surface microstructures of fish scales forms a layer that repels oil. The trapped water layer makes the surfaces of the scales underwater superoleophobic, giving the fish an oil-repellent skin. Following this strategy, many mesh and porous materials that are underwater superoleophobic have been fabricated, and these materials have been successfully applied in oil–water separation.[18–25] For example, Jiang and co-workers coated microscale porous stainless steel mesh with a nanostructured hydrogel to give a novel underwater superoleophobic rough mesh.[18] This hydrogel-coated mesh efficiently removed water from water–oil mixtures and did not become fouled with oil. Jin and co-workers fabricated a $Cu(OH)_2$ copper mesh with a nanowire-hair microstructure, and this material was superhydrophilic and underwater superoleophobic.[12] This rough mesh had a high separation capacity for both water-rich immiscible mixtures and dispersed oil–water mixtures. Zhang and co-workers described an underwater superoleophobic porous nitrocellulose membrane with both microscale and nanoscale pores.[19] The membrane had a high oil–water separation efficiency, even in a corrosive liquid environment. Although this route has proven to be effective in the laboratory, some difficulties and challenges still remain for using them for practical applications. Problems that have not been adequately addressed are the cost of the materials, the equipment required, and the preparation processes required – all of which prevent large-scale applications. Another issue is that the most widely used materials are metal meshes and porous polymers that have rough microscale–nanoscale hierarchical structures, which are generally formed using chemical corrosion or other chemical methods,[20–25] meaning that solving one environmental problem (oil pollution) could cause another (disposing of the waste produced to create the superoleophobic material). It is therefore very important that we develop or find stable materials that are underwater superoleophobic and can be used to simply, cheaply, and efficiently separate large amounts of oil–water mixtures.

Fish scales were the first materials that were discovered to show underwater superoleophobicity.[31] The characteristics of fish scales suggest that surfaces that are superhydrophilic in air are generally superoleophobic in water.[31–34] Deserts, which are largely uninhabitable, cover a significant area of the earth's surface. In addition, deserts are encroaching on cities where we live, and often cause air pollution when sandstorms occur. The main component of sand is silicon dioxide. Sand also contains

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several metal elements, as shown in Figure S1 of the Supporting Information. Silicon dioxide and metals usually have a high surface free energy. In addition, it is known that the sand surface contains a large number of hydroxyl groups. Its chemical composition with high surface free energy and hydroxyl groups endow the sand surface with intrinsic hydrophilicity. Dry sand has a tremendous ability to absorb rain. The excellent hydrophilic property of sand suggest that sand may be superoleophobic underwater and could possibly be used to separate oil and water.

In this study we show that sand shows quasi-underwater superoleophobicity and ultralow oil-adhesion for various oils upon immersion of sand in water. Those properties arise from the excellent water absorption capacity of sand. By making use of the underwater superoleophobic properties, a pre-wetted sand layer was successfully applied in oil–water separation. The good separation effect demonstrates that this strategy for oil–water separation is feasible for use in "real life" applications.

The sand used in our experiments was directly obtained from the Tengger Desert (**Figure 1**a). Figure 1c–e show scanning electron microscopy (SEM) images of the sand. The sand particles have diameters of 130–270 µm. The surface of the sand particle is not smooth, but has a microscale rough texture (Figure 1d). In addition, abundant nanoscale particles and debris distribute randomly over the sand surface (Figure 1e). Figure S2 of the Supporting Information shows the 3D and cross-sectional profiles of a single sand particle. The measured surface roughness is 49–75 nm. The sand layer forms a typical three-level roughness structure, i.e., with macroscale, microscale, and nanoscale roughness. There are large empty spaces between the sand particles. A water droplet falling onto sand-covered ground quickly infiltrates the sand, i.e., in less than 0.03 s (Figure 1f

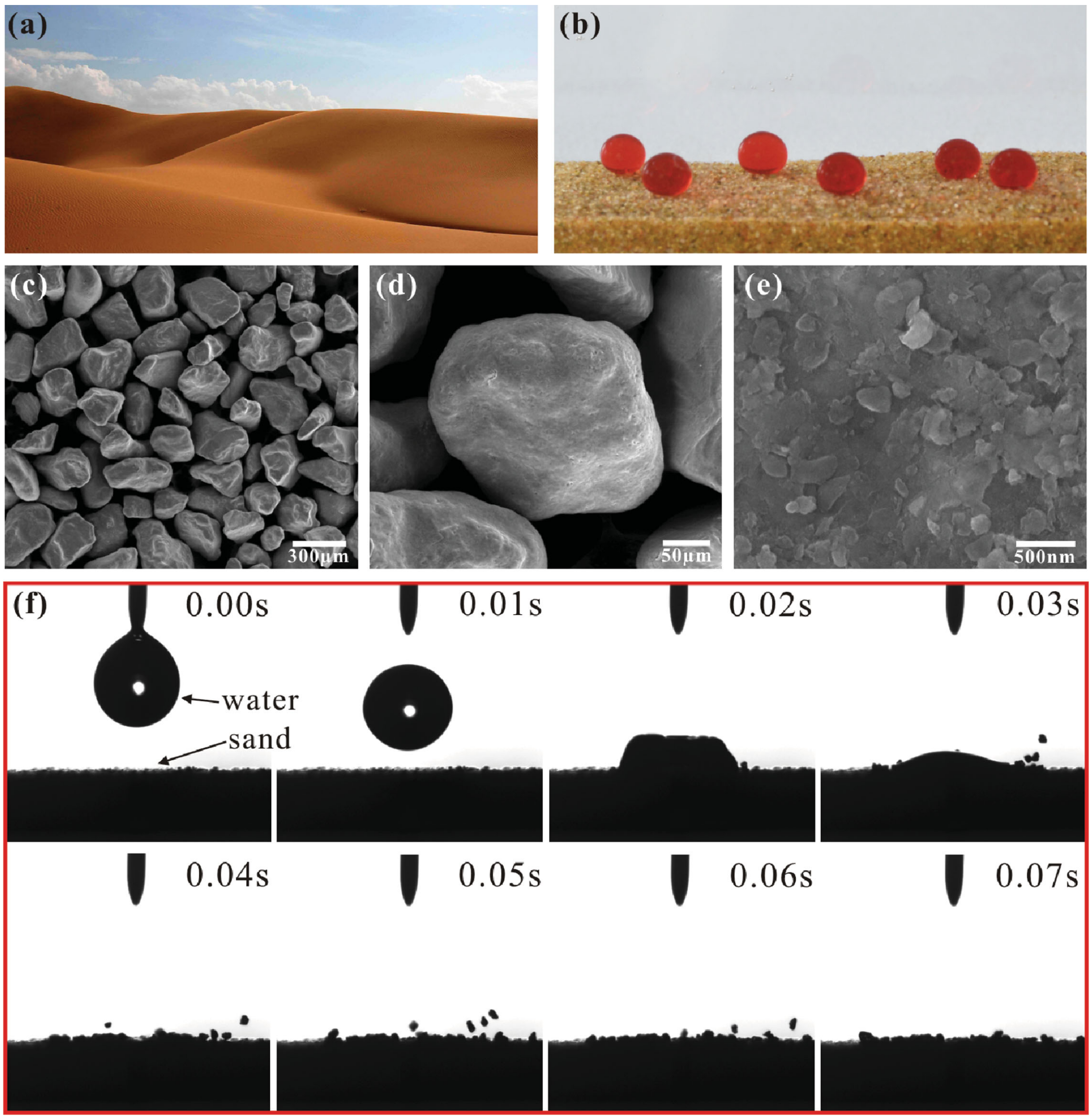


**Figure 1.** Microstructure and water absorbing ability of the sand layer. a) Photograph of the Tengger Desert. b) Photograph of oil droplets on the sand surface in water. c–e) SEM images of sand particles. f) Time series of a water droplet falling onto a sand layer in air.

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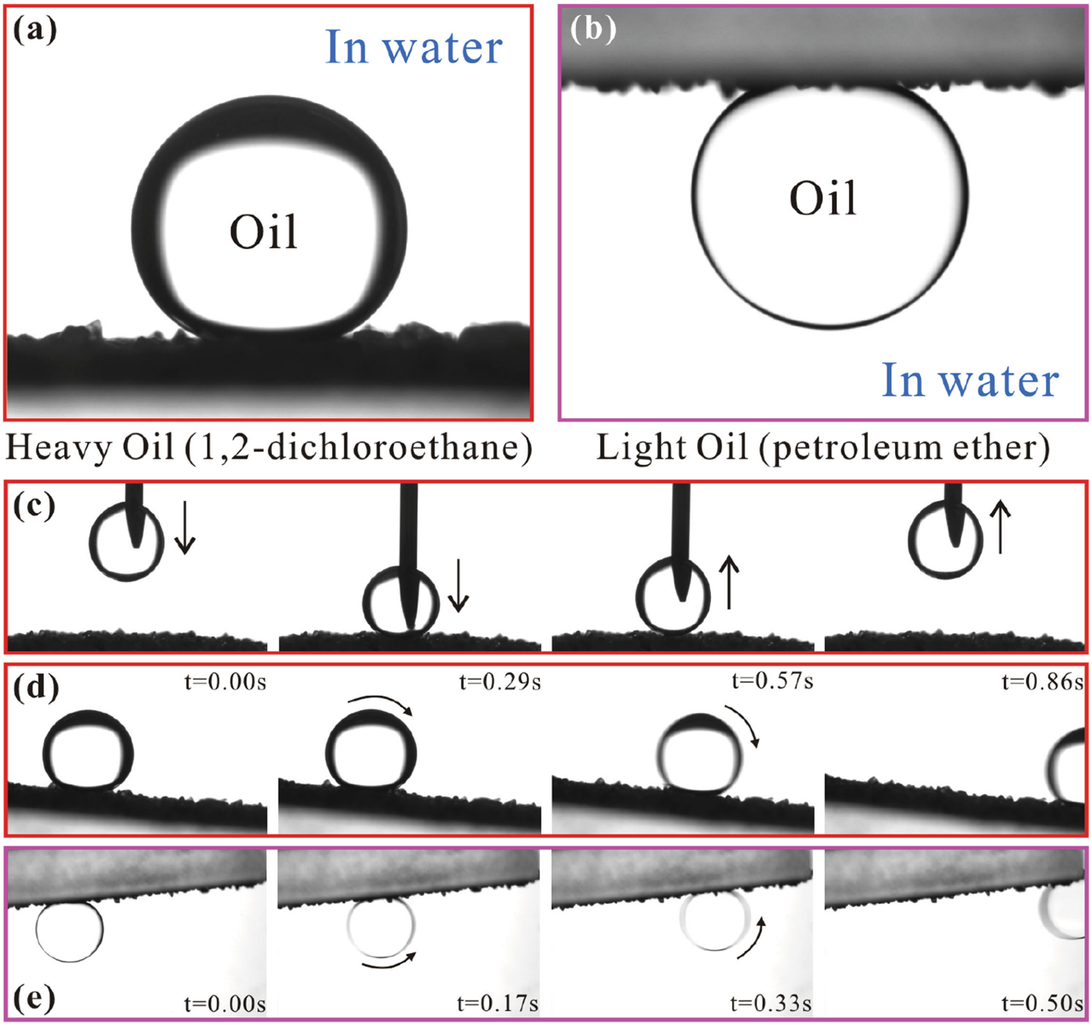


**Figure 2.** Quasi-underwater superhydrophobicity and ultralow oil-adhesion of a sand layer in water. a) Heavy oil (1,2-dichloroethane) droplet and b) light oil (petroleum ether) droplet on a layer of sand in water medium. c) An underwater heavy oil droplet making contact with and losing contact with a sand layer. d) Heavy oil droplet and e) light oil droplet rolling on a tilted sand layer in water.

and Movie S1 in the Supporting Information). This amazing permeation velocity indicates that sand is superhydrophilic.

Figures 1b and 2a show droplets of heavy oil (1,2-dichloroethane) on a sand layer in water. Each oil droplet is like a small sphere, and the OCA is 148.5° ± 2.5°, very close to the superoleophobicity criterion. It proved to be very difficult for a small underwater oil droplet to become attached to the sand surface. The process that occurred when a 7 µL oil droplet suspended on a microsyringe made contact with and then lost contact with the sand surface is shown in Figure 2c and Movie S2, Supporting Information. After touching the sand, the underwater oil droplet was repelled from the surface of the sand and was removed when the microsyringe was raised. The oil droplet did not leave the needle during the entire process, remained almost spherical and did not lose any mass, indicating that ultralow adhesion occurred between the oil droplet and the sand under water. The adhesive force was as low as 5.5 µN. Only underwater oil droplets with volumes of 8 µL and more could be placed onto the sand surface through gravity. The ultralow oil-adhesion can also be verified by the dynamic properties of the oil droplet, as shown in Figure 2d. The oil droplet easily rolled off the sand surface when the surface was tilted by 5.9°, meaning that the oil sliding angle (OSA) was 5.9° (Movie S3 in the Supporting Information). In addition, the sand shows oil-repellent behavior not only for heavy oils but also light oils. Figure 2b,e show the static shape and dynamic sliding behavior of a light oil droplet (petroleum ether) on the sand surface in water medium. The OCA was 149.5° ± 2°, and the sand was also concluded to have ultralow oil-adhesion because the OSA was only 5.7° (Movie S4 in the Supporting Information). The pre-wetted sand surface shows underwater quasi-superoleophobic or superoleophobic properties and ultralow oil-adhesion for a wide range of oils (including decane, dodecane, hexadecane, sesame oil, crude oil, diesel, paraffin liquid, and chloroform), as shown in **Figure 3**. The OCA values for these oils range from 146° to 151.5°, and the OSAs are all less than 10°.

The underwater superoleophobicity and ultralow oil-adhesion indicate that an underwater oil droplet on the sand surface is in an underwater Cassie contact state.[31–34] Sand is an intrinsically superhydrophilic material that will be fully wetted (that is,


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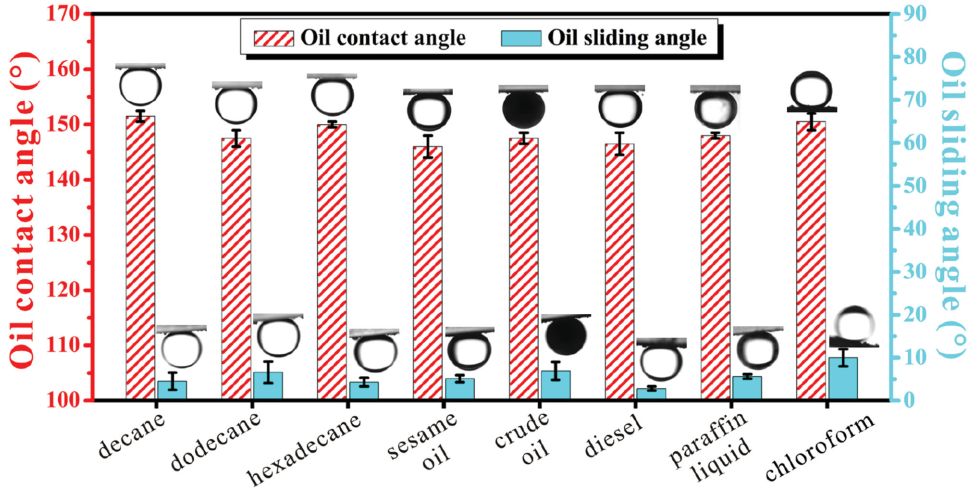


**Figure 3.** Oil contact angles and oil sliding angles for droplet of different oils on the sand layer in water medium. It shows that the sand layer is underwater quasi-superoleophobic or actually superoleophobic and has ultralow oil-adhesion.

the spaces between the sand particles will be filled with water) when immersed in water. A water cushion will form below an oil droplet placed on a sand layer in water. This cushion prevents the oil droplet from effectively making contact with the sand. The oil droplet only sits on top of the rough microstructure, forming an oil–water–sand three-phase system. Water molecules (which are polar) strongly repel oil molecules (which are non-polar), so the trapped water cushion is an ideal oil-repellent medium, endowing the sand surface with underwater superoleophobicity.[35]

The sand can be used in oil–water separation for their (quasi)underwater superoleophobicity (Movie S5, Supporting Information). As shown in **Figure 4**a, a layer of sand about 1 cm deep was fixed between two plastic tubes to act as a separating membrane. A piece of cloth was placed below the sand to prevent the sand from being lost. Before the separation process, the sand layer was pre-wetted with water. It was simply achieved by pouring a small amount of water into the upper tube (Figure 4b). A mixture of water and oil (petroleum ether) was then poured into the upper tube (Figure 4c). The water was dyed with methylene blue to obtain a blue color; the oil was dyed with Oil Red O and showed a red color. It was clear that only water could permeate the sand layer quickly and that the oil was retained in the upper tube (Figure 4d). The result demonstrates that a pre-wetted sand layer can be functionalized to serve as an oil–water separation membrane. Oil and water are immiscible. Taking advantage of the superhydrophilicity and the capillary effect of the sand layer, water can permeate and pass through the sand layer. In addition, a trapped water layer forms between the sand particles, as well as between the microstructures of the sand surface. This water layer prevents oil from permeating the sand layer, agreeing well with the underwater superoleophobicity of the pre-wetted sand layer. No external force other than gravity acted on the system during the separation process. The separation efficiency of the pre-wetted sand layer was investigated by an optical microscope, as shown in Figure S3 of the Supporting Information. The pre-wetted sand layer showed very high separation efficiency for the mixture of oil and water. The surprising ability of the sand layer to separate oil and water is mainly caused by its strong underwater oil repellency. It is worth noting that the process of pre-wetting the sand was essential to allow the oil and water to be separated. Both water and oil percolated through the sand when the mixture was directly poured onto dry sand. Interestingly, the gravity-driven separation process can be reactivated by adding another mixture. Figure 4e–h and Movie S6 (Supporting Information) show water being poured into the upper tube just after an oil–water separation cycle had finished. The newly introduced water passed through the sand layer without any oil passing through the sand. The separation process can therefore be repeated a number of times, and the separation device can be used continuously.

The water fluxes of the pre-wetted sand layer with different thickness were calculated by measuring the time for a petroleum ether/water mixture of a certain volume (the height of the water column was 15 cm; the height of the oil column was 5 cm) to permeate through, as shown in **Figure 5**a. It can be clearly seen that the water flux decreases quickly with increasing sand thickness due to an increase of effective penetration distance. The longer penetration distance results in larger viscidity resistance. When the thickness of the sand layer is 0.5 cm, the water flux can reach up to 9648 L $m^{-2}h^{-1}$. To obtain a maximum separation speed, the used sand layer should be as thin as possible to meet the requirements for effective oil–water separation. The thickness also has an important influence on the intrusion pressure of oil, which can be accurately assessed by the maximum supporting height of the oil column. As shown in Figure 5b, the maximum oil (petroleum ether) column height increases with the increase of the thickness of the sand layer. This can be attributed to thicker sand layers being detrimental to the permeation of water, while meanwhile leading to an increase of the thickness of the trapped water layer, which can provide enough surface tension to support too much oil. The water flux and the maximum supporting height of the oil column have a contrary change trend, agreeing well with Wen's work.[35]

It should be noted that our separation method is a "water-removal" process; that is, the performance of the pre-wetted sand layer only allows water in the oil–water mixture to pass


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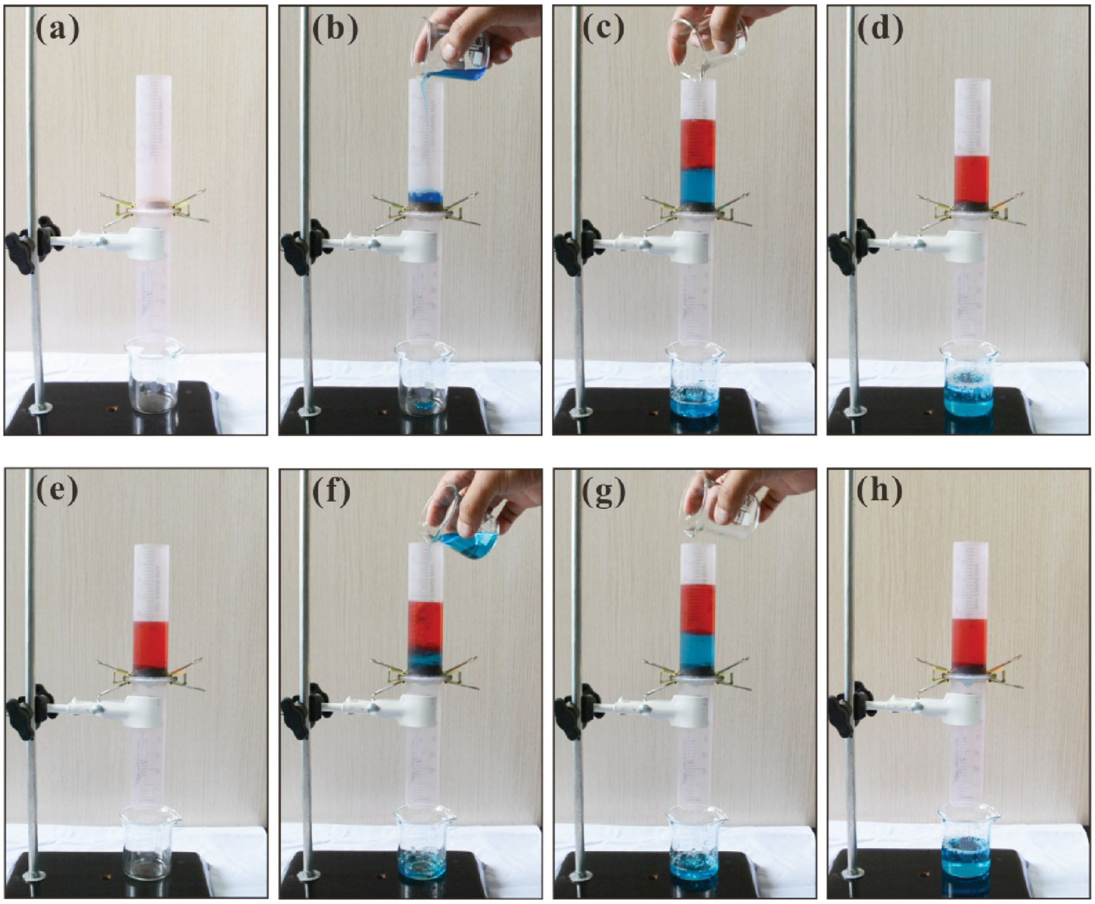


**Figure 4.** Oil–water separation study using a pre-wetted sand layer. a) Experimental setup. b) Pre-wetting the sand layer with a small amount of water. c,d) A mixture of water (blue colour) and petroleum ether (red colour) was poured into the upper tube. e–h) Restarting the oil–water separation process by adding new water to the upper tube.

through and prevents oil from passing through. Therefore, the device shown in Figure 4 can only separate a mixture of light oil and water although most of the oils in our daily life are lighter than water. This device is not suitable for mixtures of heavy oil and water since the heavy oil settles below the water, creating a layer of oil between the water and the sand layer. The oil layer prevents the water from maintaining contact with the sand layer. A U-shaped sand ridge can be used to address the separation of this type of mixtures, as shown in **Figure 6**. The sand is first piled up as a U-shaped ridge. Then, the sand ridge is pre-wetted with water. Because of the superhydrophilicity and capillary action, even the top part of the sand ridge can be wetted.[36] Finally, the mixture of heavy oil and water is pured into the valley of the pre-wetted U-shaped sand ridge.

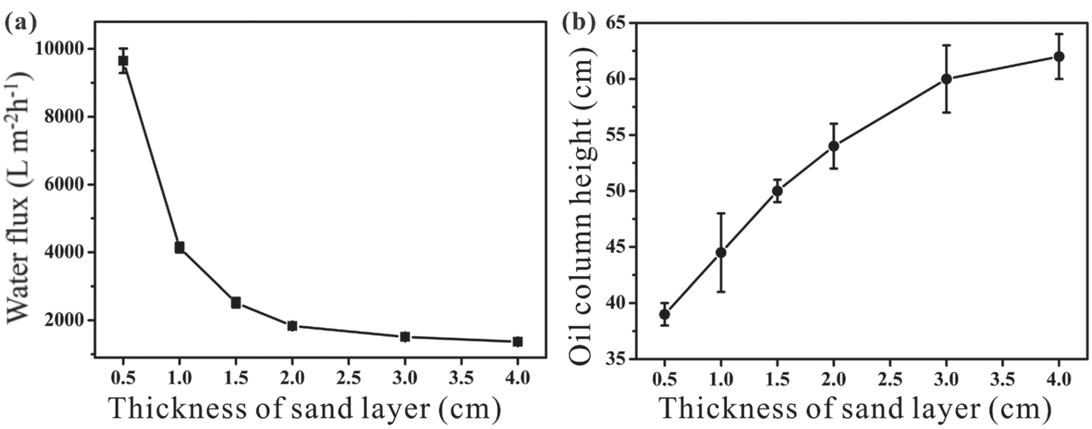


**Figure 5.** Influence of the thickness of the pre-wetted sand layer on a) the water flux and b) the maximum supporting height of the oil column.


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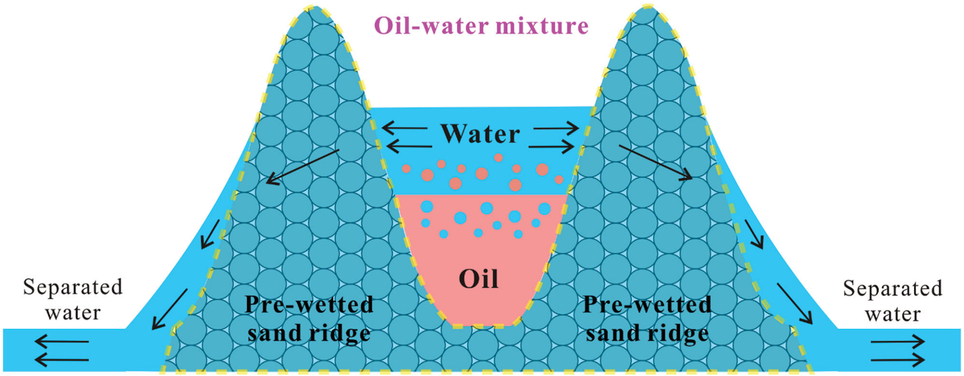


**Figure 6.** Schematic illustration of separating a mixture of heavy oils and water based on a pre-wetted U-shaped sand ridge.

Although the oil settles below the water, the water in the oil–water mixture can pass through the side well of the pre-wetted sand ridge, thereby achieving oil–water separation. In fact, this separation is also a gravity-driven process. Furthermore, this U-shaped sand ridge can separate not only heavy oil mixtures but also light oil mixtures.

In conclusion, we have demonstrated that sand shows (quasi) underwater superoleophobicity with ultralow oil-adhesion due to its powerful water absorbing ability. An oil–water–sand three-phase system formed when an oil droplet was placed on a sand layer immersed in water, and the oil droplet was in an underwater Cassie wetting state. Taking advantage of the underwater superoleophobicity, a pre-wetted sand layer was successfully used for oil–water separation. Our system showed an extremely high separation efficiency and separation capacity. Suitable sand for use in such separations can be directly obtained from desert environments and does not need to be treated before use. This simple, almost free, green, large-scale, and highly efficient route of separating oil and water offers a new perspective on practically solving pollution problems caused by oily industrial wastewater and oil spills.

## Experimental Section

*Material*: Sand was directly obtained from the Tengger desert. The sand was not done any treatment but cleaned by water before performing the oil–water separation experiment.

*Characterization*: The microstructure of the sand surface was analyzed by a Quantan 250 FEG scanning electron microscope (FEI, America). The 3D and cross-sectional profiles and the surface roughness of a single sand particle were investigated by laser confocal microscopy (LEXT-OLS4000, Olympus, Japan). The static contact angle and dynamic sliding angle were measured by a JC2000D4 contact-angle system (Powereach, China), and average values were measured five different points on the same surface. 1,2-dichloroethane ($C_2H_4Cl_2$) and petroleum ether were used as the main detecting oil. The oil–water separation efficiency of the pre-wetted sand layer was investigated by optical microscopy (CX31, Olympus, Japan).

*Oil–Water Separation*: A layer of sand was fixed between two plastic tubes with a diameter of 30 mm to act as a separating membrane. A piece of cloth was placed below the sand to prevent the sand from being lost. Before the separation process, a small amount of water was poured into the upper tube to pre-wet the sand layer. Then, the mixture of water and oil (petroleum ether) was poured into the upper tube and the separation was achieved driven by gravity. For observing the seprartion process more clearly, the water was dyed with methylene blue and showed a blue color, while the oil was dyed with Oil Red O and showed a red color.

## Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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