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All 3D Printed Superhydrophobic/Oleophilic Membrane for Robotic Oil Recycling

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Keywords: 3D Printing, superhydrophobic, oil separation, graphene, laser

Abstract

Advanced materials with high oil recycling capability plays a crucial role for rescuing marine lives from oil spill catastrophe. Existing absorption and filtration method can partially solve the challenge, however, a highly recyclable, low energy cost, and environmentally friendly method for collecting oil on open water is still missing. Herein, we propose a novel concept, using newly developed membrane for collecting oil, with surface tension confinement and gravity. Using a 3D printed superhydrophobic and oleophilic membrane, this self-floating device can selectively collect oil on water surfaces. The device can be automatically driven by a robot and achieves outstanding reusability toward oil recycling. This novel chemical concept will enable future research development of oil water separation and oil recycling.

1. Introduction

Oil pollution has a great environmental cost all over the world.[1] Many aquatic animals suffer from oil spills and the byproducts, leading to severe health problems and even death.[2] Oily water from industrial production can also cause negative eco-system impact.[3] Oil recycling techniques are important for cleaning up the oil for reuse and recovery of the eco-environment.[4]

Existing oil recycling techniques can be classed into two categories: absorption and filtration.[5] Oil absorption currently is the most widely used method for cleaning up oil worldwide. Porous sorbents can efficiently absorb large amounts of oil floating on water surfaces,[6] however, the sorbents after the absorption of oil can rarely be reused. In addition, the absorbed oil is difficult to recycle and the sorbents also might induce a negative environmental impact.[7] Novel 3D porous materials such as aerogels, sponges and foams have been studied to address these challenges. Polymer sponges such as melamine and polyurethane have been investigated for the absorption of oil.[8] Silicone sponges[9] and aerogels[10] have also been surface-modified for oil absorbing purposes. The metal organic framework (MOF) is a novel type of functional material with 3D porous structure, demonstrating high oil absorbing capability.[11] Although magnetic recycling has been demonstrated with laser reduced MOF, the reuse of such recycled oil is still challenging.[12] Filtration is another oil recycling method using porous media with superwetting properties.[13] Compared with absorption, the filtration method usually provides better reusability for the membrane and the recycled oil. Various methods have been reported for preparing these superwetting filters. Chemical etching has been used for preparing superwetting copper meshes for oil filtration.[14] Nanotubes with superhydrophobic wetting have also been studied for filtering oil/water mixtures.[15] Polymer membranes also demonstrate outstanding oil/water filtration performance with superhydrophobic modification.[16] However, to the best of our knowledge, these filtration methods are based on in-lab scale studies, using glassware. It is challenging to directly use these filters for oil recycling in open water areas.

Herein, we propose a novel 3D printed oil recycling concept by utilizing the weight of the oil for recycling through the oil-selective membrane. Using this print-on-demand technique, the functional superhydrophobic graphene could be additively printed on porous nickel foams directly, without any wet or solvent processes. With the aid of a 3D printed holder, the superhydrophobic/oleophilic membrane can float on the surface of water. The surrounding oil can automatically drift into the recycling tube by gravity, while the water cannot permeate due to the surface tension of the superhydrophobic confinement.[17] This all-3D-printed device can be automatically deployed and recovered with high reusability using robotics, which is significantly greener than existing methods.

2. Results and Discussion

The wetting and structural properties of the graphene/nickel membrane were experimentally studied and shown in **Figure 1**. The membrane is superhydrophobic for water, with the static water contact angle at 142°, as shown in Figure 1(a), and is oleophilic for oil with the contact angle of 46°, as shown in Figure 1(b).Due to the porous structure of the membrane, the oil droplet was quickly absorbed by the membrane. The chemical composition of the coating on nickel foam was characterized to be few-layer graphene by Raman spectrum, with significant D, G and 2D peak, as shown in Figure S1. To examine the microstructures of this membrane, SEM characterization was performed. The plan view SEM image revealed the porous morphologies of the nickel foam and a uniform coating of graphene, as shown in Figure 1(c). With the zoom-in observation, as shown in Figure 1(d), a hairy coating of graphene flakes was observed with mesoporous structures. These unique morphologies of the graphene flakes can ease the absorption and flow of oil droplets, while maintain the superhydrophobic surface confinement for water.

To utilize the superhydrophobic/oleophilic properties of this membrane, a gravity driven oil separation concept is proposed, as in Figure 2. After the 3D printing of graphene onto nickel foam, the composite membrane is bended to a tube, as shown in Figure 2(a). Then a reservoir tube is chosen according to the size of the roll, and the corresponding floating holder is printed using 3D printed thermoplastic, as shown in Figure 2(b). Next, the tube will be assembled into the roll membrane, and integrated into the floating holder. At the same time, six plastic foams pads are assembled on the floating holder, so it can steadily float on the water surface, as shown in Figure 2(c). Finally, the device is put on the water surface, for oil recycling use.

The oil and water separation mechanism of this 3D printed membrane is schematically illustrated in Figure 3. The cross-section illustration of the device after immersion below the oil and water interface is shown in Figure 3(a). Due to the impermeable characteristics of the superhydrophobic membrane, the water cannot pass the surface confined barrier. Meanwhile, the oil can permeate through the 3D printed membrane, so the oil droplets can accumulate in the bottom of the tube, as shown in Figure 3(b). If the superhydrophobic/oleophilic properties of the membrane do not change over time, more oil will accumulate into the tube without water, as shown in Figure 3(c). Eventually, all the oil can be collected, as shown in Figure 3(d).

Experimentally, the above hypothesis was tested, as shown in Figure 4. The blue color plastic floating holder was deliberately removed to illustrate the oil recycling process. The 3D printed membrane with the recycling tube was immersed below water level, as shown in Figure 4(a). Orange color oil was then added into the water, as shown in the red dashed line area of Figure 4(b). As soon as the oil was added, the oil started to permeate through the membrane, and a significant volume of oil was collected within the first minute, as shown in the lower dashed red line area in Figure 4(c). After around 20 minutes, almost all the oil was recycled, except the oil stuck to the inner edge of the outer bottle, as shown in Figure 4(d).

The reusability of this 3D printed membrane was also experimentally examined, as shown in Figure 5. In this, 3.5 mL of oil was initially added to a bottle, as shown in Figure 5(a). In the first recycle test, almost all the 3.5 mL oil was collected in the recycle tube, as shown in Figure 5(b), and after 10 cycles of recycling, there was no significant decrease of the collected volume observed, as shown in Figure 5(c). The lattice matching between the graphene and the nickel provides a solid mechanical bonding[18], so even after 100 cycles of recycling, the graphene can still be firmly retained on the nickel foam, as shown in Figure S2.[19] Hence, a high reusability of the 3D printed oil recycling membrane was demonstrated. The 3D printed floated holder is shown in Figure 5(d).

The floating ability of this oil recycling system was tested as shown in Figure 6. A commercial ABB industrial robot was used to illustrate the deployment and collection of the 3D printed oil recycling device, as shown in Figure 6(a). A plastic handle was connected to the 3D printed holder for ease of the robotic grab movement, as shown in Figure 6(b), and the robot then grabbed the device above the water, as shown in Figure 6(c). After the robot delivered the device, the 3D printed system can self-float on the surface of the water, as shown in Figure 6(d). For collection of the device, the robot reached for the white plastic, as shown in Figure 6(e). After collecting the device, the robot eventually placed the device in the desired location, as shown in Figure 6(f), so the capability of robotic deployment of this 3D printed self-floating oil recycling system was verified. The complete video of the robotic deploy and collect process is given in the supplementary information.

Using additive manufacturing technologies and the superwetting properties of the coating, this oil recycling concept was experimentally demonstrated, and was proven to have several advantages over existing methods. Compared to existing oil absorbent materials, this oil filter membrane exhibits outstanding recycling capability for both the membrane as well as the recycled oil.[20] It can also be fully automatedly using a robot, with artificially 3D printing designs. There are also a few more advantages compared to existing oil filtration methods. Many polymers have shown outstanding superhydrophobic and oleophilic properties,[21] however, the use of fluorine might induce environmentally side effects, compared to our green approach.[22] Electrospun polystyrene membranes possess superhydrophobic and superoleophilic properties, however, the electron spinning process lack the scalability compared to our industrial capable mass production methods.[23] In addition, the use of a solvent during the processing of these polymers will generate organic waste. This 3D printing technique place the functional graphene only at the desired location, without any additional waste generated. The self-floating device can function on open water areas independently, with no need for any manual operation.[24] The hollow structures of the thermoplastic holder can effectively avoid the influence of hydrophobicity (as measured of 72o water contact angle in Figure S3)of the PLA material. The gravity driven recycling method also avoids using external energy during the oil recycling process, which can significantly reduce the associated carbon emissions. Therefore, this 3D printed graphene/nickel hydrophobic/oleophilic membrane is significantly greener to other oil separation methods.

However, there are some limitations of the current study. The real wastewater could contain more complicated conditions. Although the graphene/nickel foam membrane can sustain high performance in neutral or even alkaline conditions, it is challenging to directly use these membranes in acid environments. In addition, the existing of microparticles in real water might block the porous structures of the membrane, additional filters are needed before the oil/water separation process.

3. Conclusions

An environmentally friendly oil collecting method is developed and verified, using additive manufactured graphene and robotic recycling. This system has many green features, such as high reusability, zero waste, zero use of solvents and fluorine. The self-floating attributes open up a new field for deploying oil filtration recycling in open water. Future work can be performed on using other superhydrophobic and superoleophilic materials, with higher oil flow rate for faster oil recycling speeds.

4. Experimental Section

Polyimide films of 50 μm thickness were used as the precursors for the superhydrophobic and oleophilic graphene. Nickel foam with 1 mm thickness was used directly after purchase, without any surface treatment. The polyimide film was placed above the nickel foam, so the laser can photochemically convert the aromatic rings of polyimide molecule into graphene, and simultaneously push the synthesized graphene onto the underlying nickel foam. The graphene coating was deposited onto the nickel foam by directly focusing a 4 W laser at 1064 nm wavelength, using a 400 mm/s scanning speed, according to the designed pathway for the laser beam using the laser induced forward transfer strategy.[25] The mechanical holder was designed using Autodesk AutoCAD and printed using a MakerBot FDM 3D printer. The Raman spectrum was performed using a LabRAM HR 800 Raman Spectrometer with a 488 nm laser source. The water wetting properties of the membrane were tested using a Sedate 100SB optical contact angle meter using the sessile drop method. The oil wetting properties of the membrane was studied using a USB camera. The microstructures of the graphene on the nickel form were characterized using a scanning electron microscope (SEM), model Rescan VEGA3.

Supporting Information

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

Acknowledgements

G. Li acknowledges the funding support (1-BBX9) of Partner State Key Laboratories in Hong Kong from the Innovation and Technology Commission (ITF) of the Government of the Hong Kong Special administrative Region (HKSAR), China. K.C. Chan acknowledges the grant from the Research Grants Council of the Hong Kong Special Administrative Region, China (Project No. PolyU 15222017).

Received: ((will be filled in by the editorial staff))
Revised: ((will be filled in by the editorial staff))
Published online: ((will be filled in by the editorial staff))

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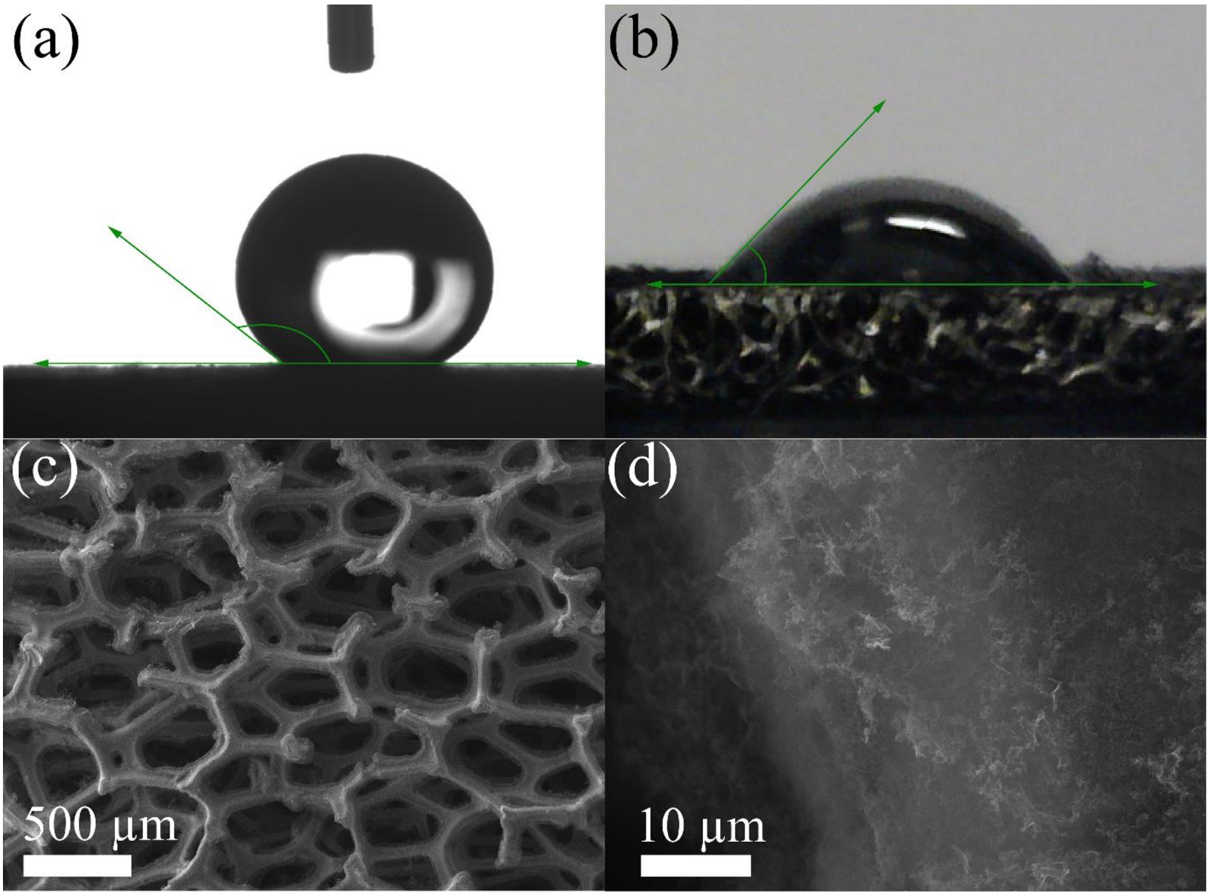


Figure 1 Characterization of 3D printed superhydrophobic/oleophilic membrane. (a) Contact angle of water on the membrane. (b) Contact angle of oil on the membrane. (c) SEM image of the membrane. (d) Zoom-in SEM image of the membrane.

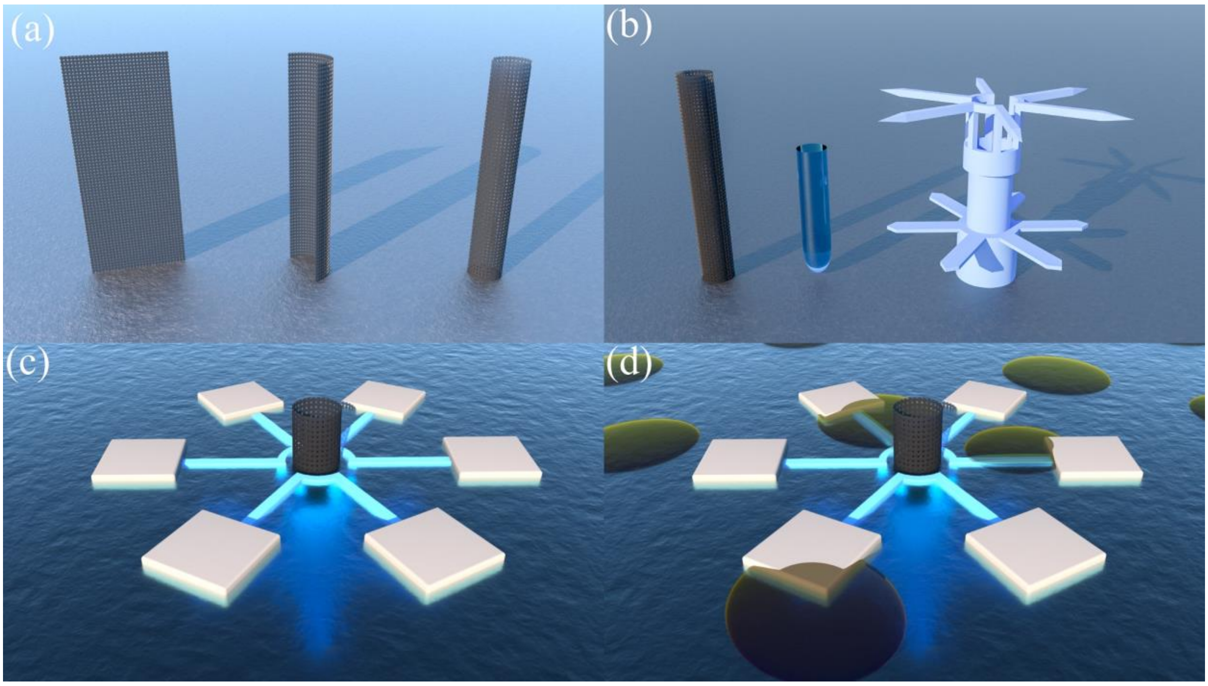


Figure 2 Schematic Illustration of 3D printed superhydrophobic/oleophilic oil recycling device. (a) Membrane bending to tube shape. (b) Rolled membrane, recycling tube, and thermoplastic printed floating device. (c) Self-floating oil recycling device. (d) Oil recycling process of the device.

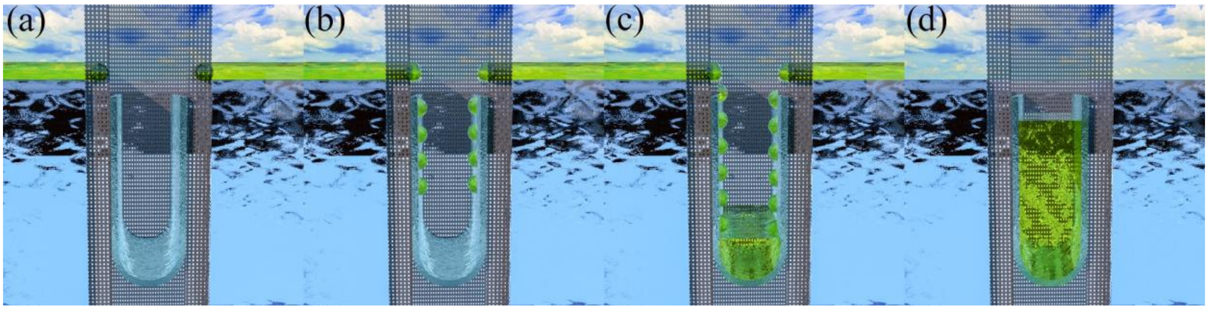


Figure 3 Cross-section illustration of the oil recycling process of the 3D printed membrane. (a) When the device just immerged under water and oil interface. (b) The oil droplet starts to flow into the tube. (c) The collected oil filled the tube. (d) The oil above water can be fully collected within the tube.

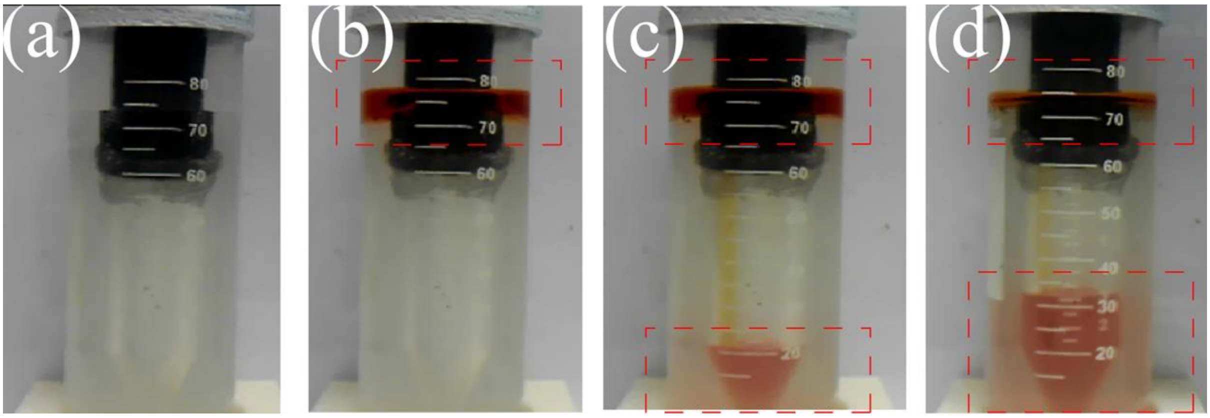


Figure 4 Optical image of the 3D printed membrane for recycling of oil according to different time. (a) Initial status without oil. (b) The start moment with added oil. (c) 1 min after the oil was added, oil observed in the recycling inner tube. (d) 20 min after the oil was added, all the oil was recycled, except the one adhesive on the surface of the outer bottle.

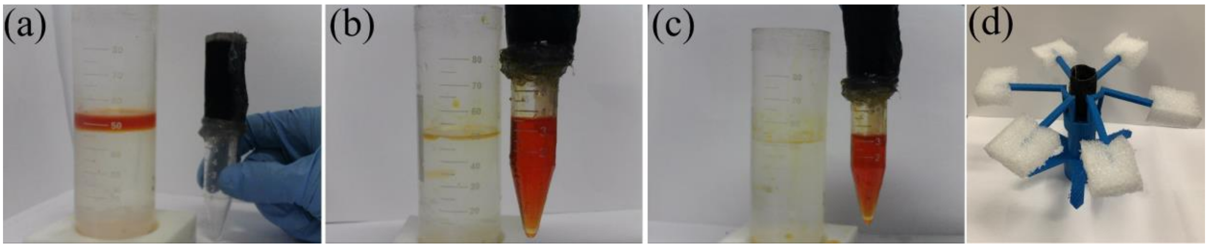


Figure 5 Reusability test of the oil recycling system. (a) 3.5 mL added to the bottle. (b) After first recycle, almost all the oil was recycled in the tube. (c) After 10 times recycle, still all the oil can be recycled. (d) Photo of the self-floating device for recycling of the oil.

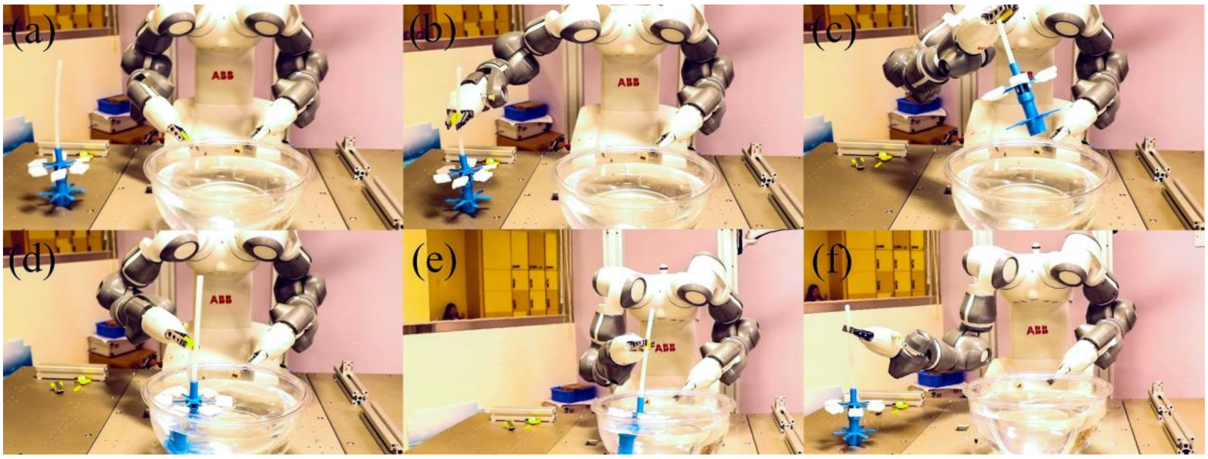


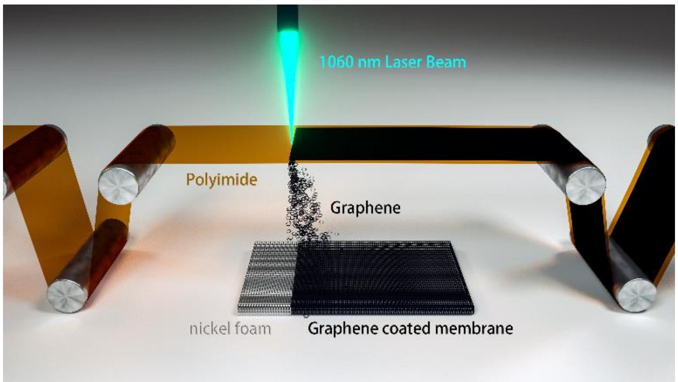
Figure 6 Photo of deploy and collect the oil recycle device by robot. (a) Initial state. (b) The robot grabbed the device. (c) The robot lifted the device above the water. (d) The device was dropped into the water (e) The robot picked up the device from the water (f) The robot put the device to the desired location.

The table of contents entry: 3D printed superhydrophobic and oleophilic oil-separation membrane can efficiently recycle oil spill.

Keyword: 3D Printing, superhydrophobic, oil separation, graphene, laser

Dr. G. Li[1,2], X. Mo[1], Y. Wang[1], Dr. C.-Y. Chan[1] and Prof. K. C. Chan[1*]

All 3D Printed Superhydrophobic/Oleophilic Membrane for Robotic Oil Recycling



Supporting Information

All 3D Printed Superhydrophobic/Oleophilic Membrane for Robotic Oil Recycling

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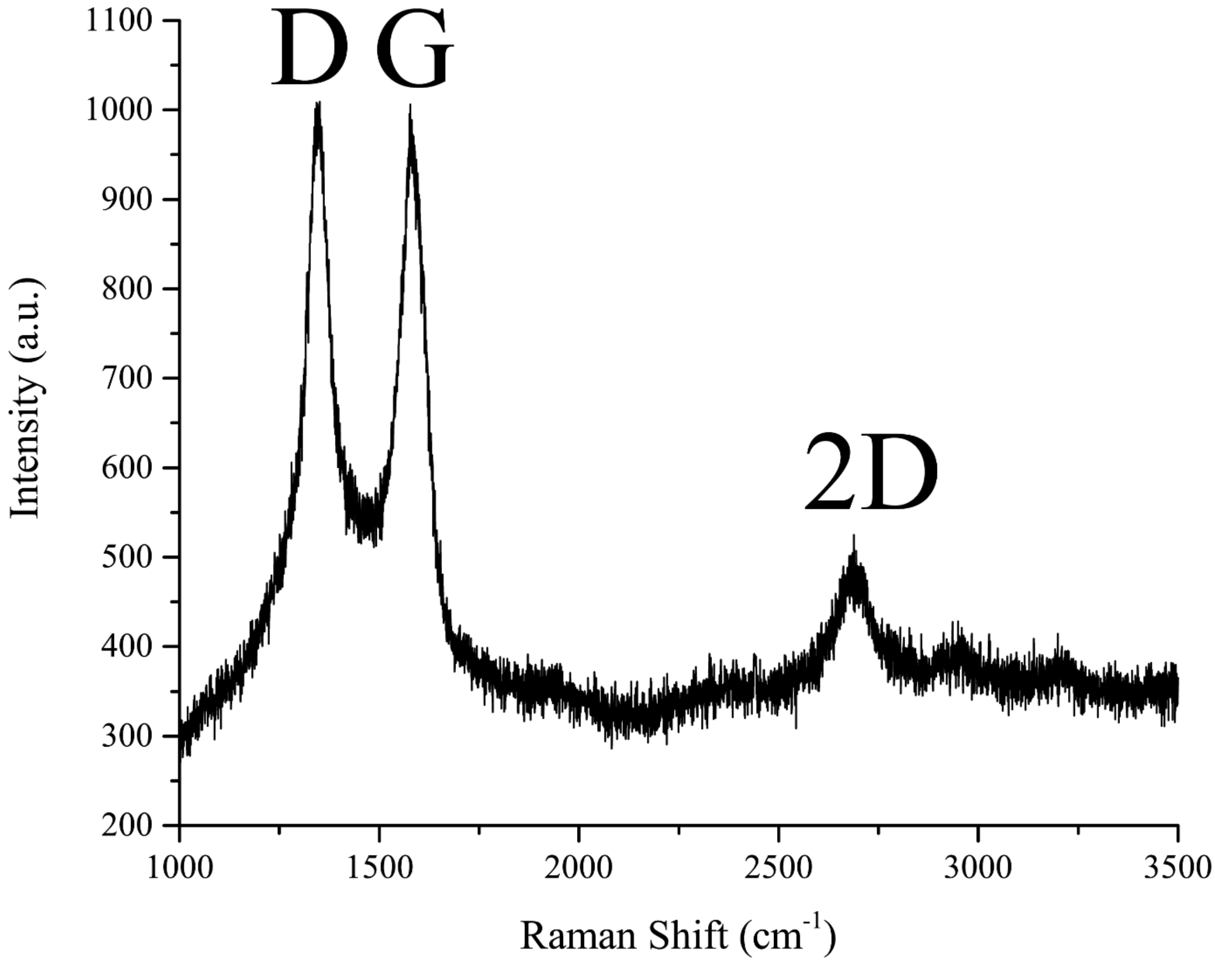

Figure S1 Raman characterization of graphene on nickel foam.

Figure S2 Image of graphene/nickel foam membrane after 100 cycles of oil separation.

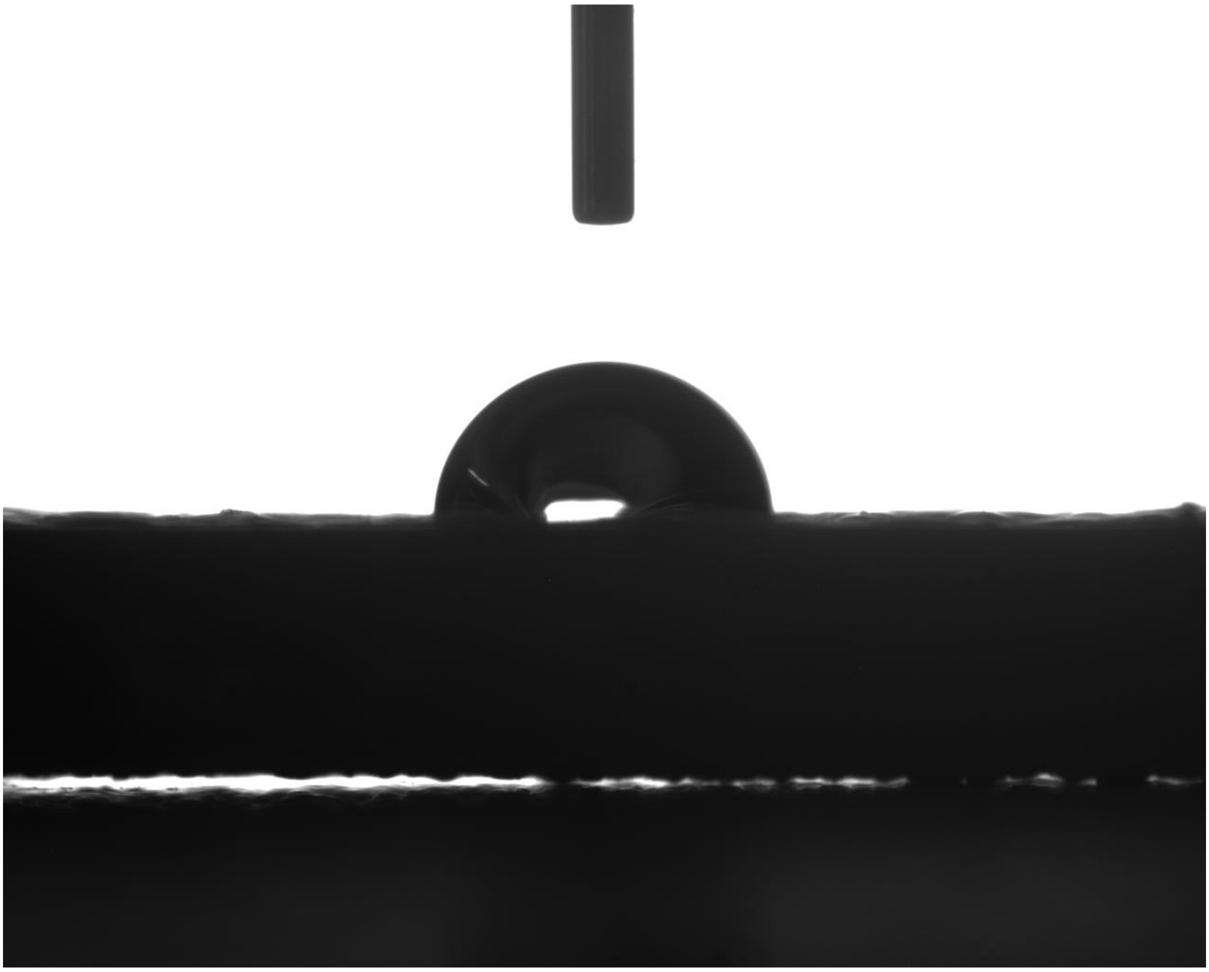

Figure S3 Water contact angle on the thermoplastic holder.