Magnetic and highly reusable macroporous superhydrophobic/superoleophilic PDMS/MWNTs nanocomposite for oils sorption from water

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ABSTRACT Oil/water separation is a worldwide challenge to prevent serious environmental pollution. Development of sorbent materials with high selectivity, sorption capacity, easy collection and recyclability is demanding for spilled oil recovery. In this field, magnetic controllable superhydrophobic/superoleophilic materials have received broad attention due to the possibility of easily being driven to polluted area and recovered by simple magnetic interaction. However most of the proposed materials exhibited low reusability, low oil uptake ability and low mechanical properties. Moreover their synthesis is complex and expensive. Here we propose for the first time

the fabrication of a porous reusable magnetic nanocomposite based on polydimethilsiloxane (PDMS) and multiwalled carbon nanotubes (MWNTs) via a low cost and facile hard template approach. The material can selectively collect oil and organic solvents from water surface and heavy oil under water reaching the equilibrium in less than two minutes and being capable to adsorb oil least two times more quickly than other PDMS based porous materials. Depending on the oil type, the sorption capacity (absorbency) of PDMS-MWNTs sponge is in the range of 850% to 2000% with respect to the initial weight of the sponges. Furthermore the materials evidenced excellent mechanical properties with a stress at 60% strain 10 times higher with respect to other proposed porous systems for oil sorption and maintaining its characteristics after 50 cycles at 90% strain, along with high thermal and chemical stability and high reusability, all features that make them useful high-performance systems for plugging oil leakage.

In recent years, oil-spill accidents and leakage of organic liquids have caused ecological problems, including nearly irreversible damage to ecological systems with big consequences in economic, social and health fields.[1–3] Different methods have been proposed and used to recover organic liquids dispersed in water such as physical sorption by sorbent materials, mechanical recovery by oil skimmers,[4,5] in situ burning,[6] physical diffusion,[7] filtration membrane[8–10] and biodegradation.[11] However low separation efficiency, generations of secondary pollutants and cumbersome instrumentation have caused difficulties in their practical use. To overcome these problems, the synthesis of lightweight porous oil absorbent materials is one of the most promising strategy.[12,13] Porous absorbents can concentrate oil liquid inside the pores making their transport, storage and removal from water easier. An ideal sorbent material should be (super)hydrophobic and (super)oleophilic in order to be oil selective, with a high oil sorption rate and capacity,[14] lightweight, low-cost, easily fabricated and readily reusable.[14] High recyclability of the sorbent could in fact dramatically reduce the cost of oil spill recovery. Recently, various materials have been proposed for oil/water separation such as carbon nanotubes (CNTs) sponges,[15,16] polydimethylsiloxane (PDMS) sponges,[17,18] polystyrene fibers,[19,20] graphene sponges.[21] Among them carbon and silane based materials showed higher sorption capacity and reusability. Beside the chemical affinity, the porosity of these materials plays a key role for the achievement of high oil

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sorption capacity. However, as the porosity is increased, silane and carbon based sorbents with high sorption capacity usually evidenced low mechanical strength (less than 1 kPa at 60% strain). This is very limiting for their practical application due to the fact that the viable stack height of the sorbent after adsorption is only a few centimeters.[15] Moreover the preparation process of these materials often requires complex synthetic steps and cumbersome and expensive instrumentation, which limit their practical application. PDMS sponges with fast oil absorption using sugar particles as templates have been fabricated. Although satisfactory oil uptake performances were reported, the use of vacuum apparatus or centrifuges complicates the large- scale production of the material. Moreover, in some cases sponges evidenced low stress strain (~0.05 kPa at 70% strain).

Choi et al.[18] fabricated reusable., the synthetic steps included shaping of sugar templates and. Zhang et al.[22] prepared sponges with excellent oil absorbency diluting PDMS prepolymer in p-xylene and using sugar particles as template; however, Zhao et al.[17] synthesized sponges with high oil absorption diluting PDMS in dimethicone and using sugar particles as template. Also in this case, the large-scale production of the material was prevented by the required use of centrifuges, in addition the sponges with higher absorption capacity evidenced

A recent trend in the field of water/oil separation sorbent materials is represented by the fabrication of "smart absorbents"[14] on which the absorption properties can be controlled by pH, electrical, photonic, thermal or magnetic input. Among them, magnetic-controllable materials have received broad attention in recent years due to the possibility of being easily driven to polluted area and recovered by simply exploiting magnetic interaction. To this aim, various hydrophobic materials[15,23,24] were combined with magnetic materials by adopting two strategies. The first approach consists in depositing a magnetic coating on the surface of porous materials with subsequent reduction of pore volume thus affecting sorption capacity, especially with magnetic particles larger than microns.[25] Moreover, magnetic layers are not stable typically requiring new synthetic steps to recycle the sponge.[23] The second approach consists in polymerizing superhydrophobic sponges in the presence of magnetic nanoparticles. However most of the reported materials collapse or easily fracture in compression or stretch tests.[24] In addition most of magnetic superhydrophobic spongeous materials involved complex synthetic procedures that make them scarcely suitable for practical applications.

Among the developed porous magnetic materials, PDMS has not been proposed up to now due to the difficulties in preserving mechanical properties of the sponge structure after modifications required for conferring it magnetic properties.[17]

Here we report for the first time the fabrication of a porous magnetic reusable nanocomposite integrating PDMS sponges with multi-walled CNTs (PDMS-MWNTs) via a facile hard template approach that does not require the use of complex instrumentation. The PDMS-MWNTs sponges show excellent superhydrophobicity and superoleophilicity and, importantly, higher compressibility, enhanced mechanical strength and improved thermal stability compared with PDMS alone and with other proposed porous systems for oil uptake. The magnetic sponges swell in various organic liquids with high and fast absorbency rate. Moreover, the organic liquids can be easily recovered by simply squeezing the sponges that can be thus reused without loss of function.

Results and discussion

Preparation of PDMS-MWNTs sponges

Porous PDMS-MWNTs sponges were fabricated by polymerization of the prepolymer in different solvents in the presence of GMps covered with MWNTs. A proper amount of MWNTs powder was allowed to adsorb on the surface of glucose crystals by simply mixing the two powders in dry condition overnight. In this way the impact of sugar crystals with MWNTs could mechanically break the π-π stacking between the nanotubes favoring their absorption on GMps surface.[26] The as prepared MWNTs-GMp nanocomposites were packed in a syringe and then pre-polymerized PDMS was added in the syringe and infiltrated into GMp-MWNTs microparticles. After curing, the porous PDMS-MWNTs nanocomposites were sonicated in warm water and ethanol until the washing solutions became clear (figure 1a). These steps are crucial in order to completely remove GMps and not entrapped MWNTs.
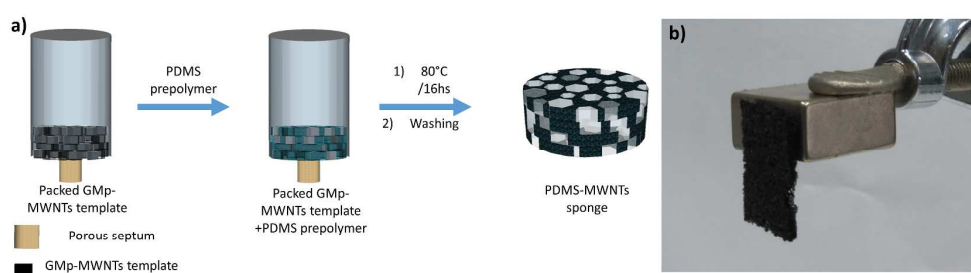

Figure 1 a) Schematic illustration of the preparation of PDMS-MWNTs sponge; b) Photograph of PDMS-MWNTs sponge anchored to a magnet

As shown in figure 1b, the as prepared PDMS-MWNTs sponges are magnetic and the simple preparation method makes their fabrication suitable for large-scale production without the need of complex and expensive equipment.

Performance of PDMS-MWNTs Oil Absorbent

The porous PDMS-MWNTs sponges have the ability to quickly take up oil. Although porous PDMS materials with these abilities have recently been synthesized,[17,18,22] none of them evidenced magnetic properties. Moreover, the influence of different solvents for prepolymer dilution on the stability and sorption capacity of the developed material was not evaluated in any case.

As detailed before, the sponges are here easily prepared in different shape and dimensions without the use of cumbersome and expensive instruments. Furthermore, different solvents and different ratios between pre-cured PDMS and solvent were used for preparing PDMS-MWNTs sponges and their oil absorbency was evaluated with the aim to select the optimal conditions determining the most satisfactory oil uptake properties.

For the tests, hexane was used as solvent to dilute pre-polymer and dichloromethane uptake was evaluated. As reported in figure 2, an absorbency higher than 700% for dichloromethane was obtained for PDMS-MWNTs sponges prepared with a ratio of 4:6 PDMS/hexane by weight, by using template particle size of 68±29 μm and 3% (by weight) of MWNTs with respect to the template. Sponges prepared with lower concentration of pre-polymer exhibited lower mechanical stability resulting in collapsing of the porous structure. From figure 2 it is clearly evident that the oil sorption increases when PDMS prepolymer concentration decreases. This could be due to a lower density of the mixture that facilitates the penetration of the reagents across the template microparticles producing a more porous structure with interconnected pores.[17]
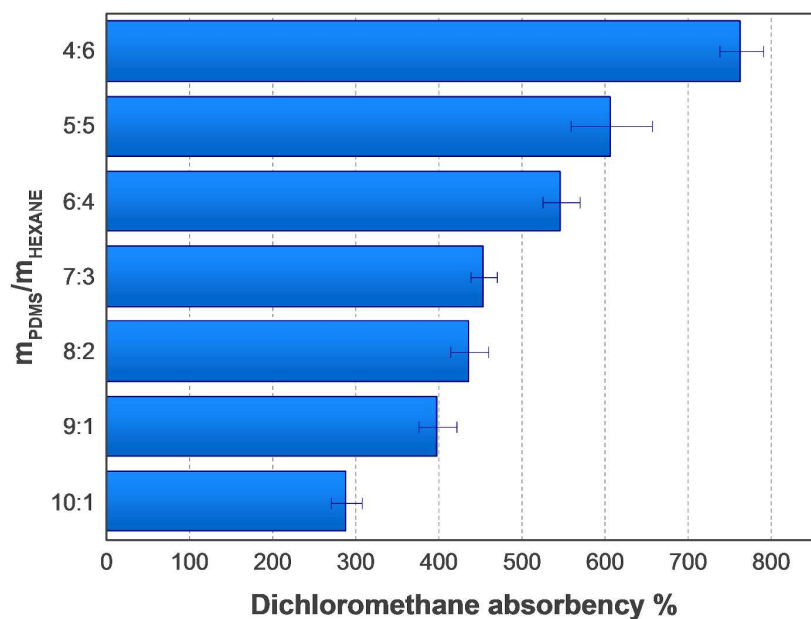
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Figure 2 Dichloromethane sorption (%) of the PDMS-MWNTs sponges with different m_{PDMS}/m_{hexane} (the size of GMps is $68\pm29\mu m$ and 3% (w/w) of MWNTs with respect to GMps is used).

The impact of solvents on PDMS-MWNTs sponge formation was evaluated by preparing different sponges with different solvents. We tested chloroform, ether, hexane and dichloromethane; 4 g of the pre-polymer were diluted in 6 mL of each solvent, and the uptake of dichloromethane was evaluated. Template particles size (68 ± 29 μm) and the amount of MWNTs (3% w/w) were maintained equal in all samples. As evidenced by figure 3, the solvent used to dilute pre-polymer has a significant effect on oil uptake process. In particular, similarly to what observed above for PDMS pre-polymer dilution, the decrease of the density of the solvent increases the absorption capacity, confirming the need to favor the penetration of the reagents across the template microparticles to achieve the formation of a highly porous structure with interconnected pores allowing an efficient absorption mechanism.
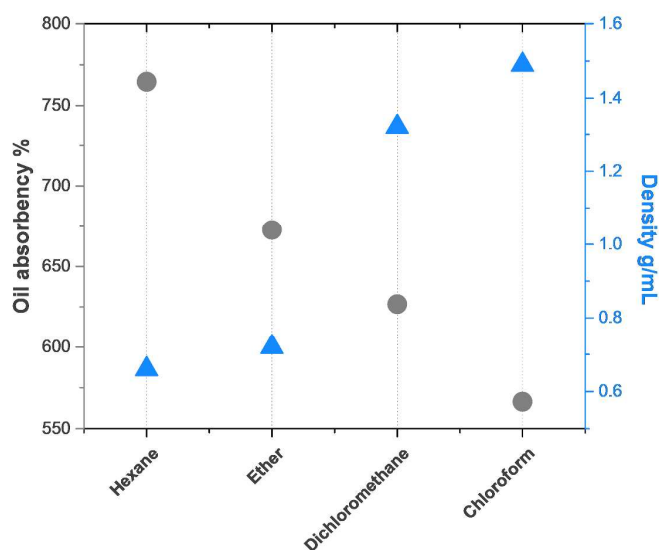
Figure 3 Variation of absorbency of the PDMS/MWNTs sponges for dichloromethane with different solvents used to dilute PDMS pre-polymer (the size of GMps is 68±29 µm and 3% (w/w) of MWNTs with respect to GMps is used)

Also the size and the kind of templates can significantly influence the porosity and thus the oil uptake performances[17,18]. For template-assisted synthesis of porous materials a common strategy to modify the dimension of pores is to use microparticles with different sizes as template. To study these aspects we prepared different PDMS-MWNTs sponges maintaining the ratio m_{PDMS}/m_{hexane} equal to 4:6, the amount of MWNTS equal to 3% (w/w) with respect to the template and using as hard template GMps with different average size, namely 68±29 µm, 230±85 µm, 620±100 µm and 3638±252 µm. Only using templates with average particle size lower than about 700 µm we were able to produce stable and well-shaped materials. Scanning electron microscopy (SEM) images of the sponges prepared in the presence of particles with an average size of 68±29 µm (fig. 4 a) and 620±100 µm (fig 4 b-c) evidenced an interconnected three dimensional (3D) framework with macropores size consistent with the size of the used hard template. Evaluating the uptake of dichloromethane of the sponges prepared with different porosity (fig. 4 e), we observed that by increasing template dimensions from 68±29 µm up to 230±85 µm the oil absorbency remains constant (~760%), while using ten times bigger GMps (620±100 µm) oil absorbency increases up to 1200%.

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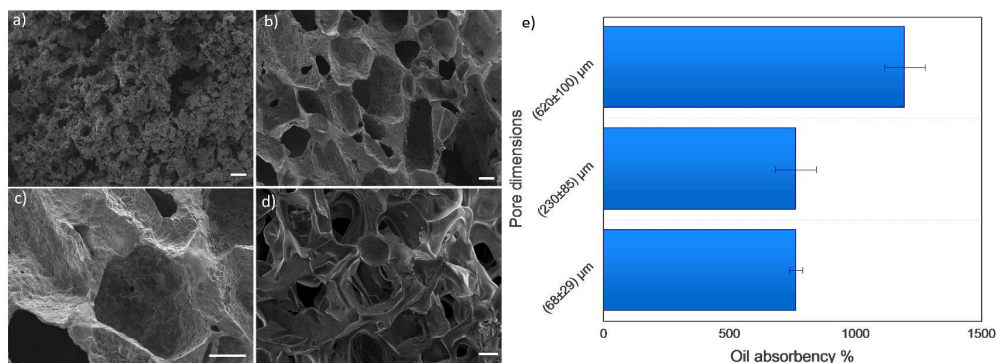**Figure 4** SEM images of porous PDMS-MWNTs with the size of GMps equal to a) 68±29 μm and b) 620±100 μm (with the relative zoom in c). d) porous PDMS with the size of GMps equal to a). Scale bar is 200 μm. e) Oil absorbency of PDMS-MWNTs sponges prepared from different templates.

Collected results suggest that bigger pores can provide larger volume for oil storage. In addition, sponges prepared in the presence of MWNTs evidenced a rougher surface with respect to porous PDMS alone (fig. 1 d) suggesting the presence of the MWNTs on and/or close to the pore surface.

The presence of MWNTs in the fabricated porous materials has a dual key role. On the one hand, they are responsible for the magnetic properties of PDMS-MWNTs sponges and, on the other hand, they possess oleophilic and hydrophobic properties,[15] large specific surface area and rougher surface thus determining an enhancement of absorption properties of PDMS-MWNTs nanocomposites sponges. With the aim to verify the contribution of MWNTs in oil uptake mechanism, different samples were prepared with different ratio of MWNTs with respect GMps maintaining m_{PDMS}/m_{hexane} equal to 4:6 and using as hard template GMps with average size of 620±100 μm. We found that increasing the amount of MWNTs from zero to 3%, the average dichloromethane uptake slightly increases from (1180±38)% to (1228±45) %, while the use of a lower amount of MWNTs (i.e. 1%) determined the same dichloromethane uptake as in the case of PDMS alone, evidencing the lack of a contribution of MWNTs in oil absorbency in this case. We observed also that with the further increase of MWNTs amount (i.e. up to 6%), the material lost consistency and stability and dichloromethane uptake decreased down to 1080%.

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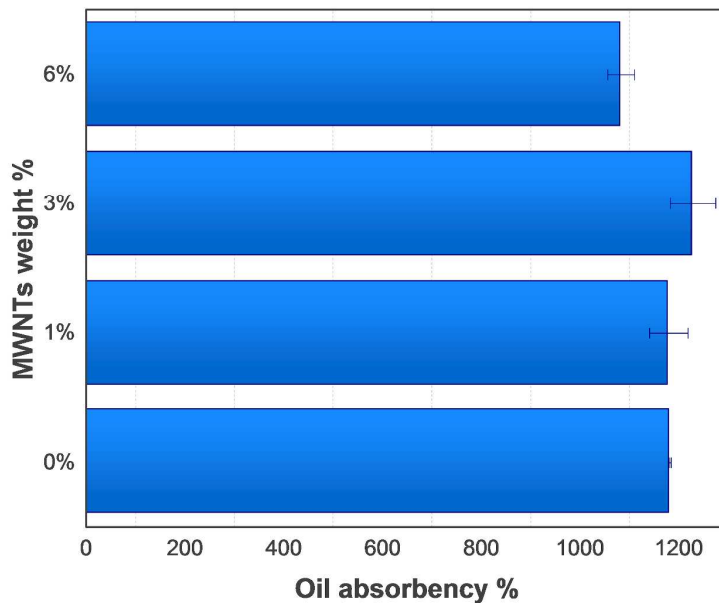45
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Figure 5 Oil absorbency of PDMS/MWNTs sponges prepared from different ratio of MWNTs with respect to GMps

The dichloromethane sorption of the sponges is plotted as a function of time in figure 6. The equilibrium is reached in few minutes as shown by the absorbency remaining constant without any significant variation, at least for the analyzed time (60 min), evidencing the fast oil absorption properties of the material. Such absorption rate is significantly higher with respect to previously reported PDMS systems,[17] for which time higher than 60 minutes was required to saturate pores with dichloromethane, thus evidencing as the proposed system can dramatically speed up oil uptake process.
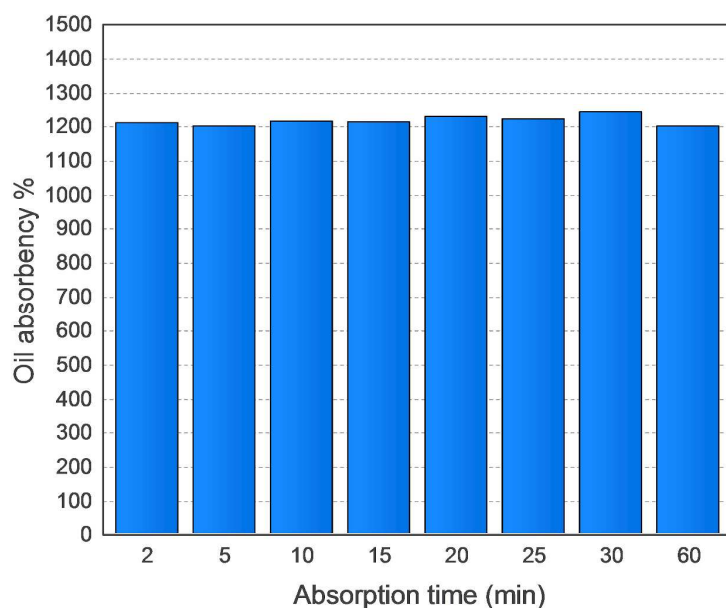
Figure 6 Oil absorbency for different contact time with PDMS-MWNTs (the size of GMps is 620±100 μm and 3% (w/w) of MWNTs with respect to GMps is used)

Figure 7 shows XPS wide scan spectra of sponges made of PDMS only (green line) and PDMS-MWNTs (red line). In both samples the peaks of Si 2p (103 eV), C 1s (285 eV) and O 1s (530 eV) are present. Si/C atomic ratio was calculated resulting equal to 0.45 in PDMS sample, in good agreement with the theoretical ratio of 0.5, and to 0.25 in PDMS-MWNTs samples, confirming the presence of MWNTs not only in the bulk of the porous PDMS but also on its surface.
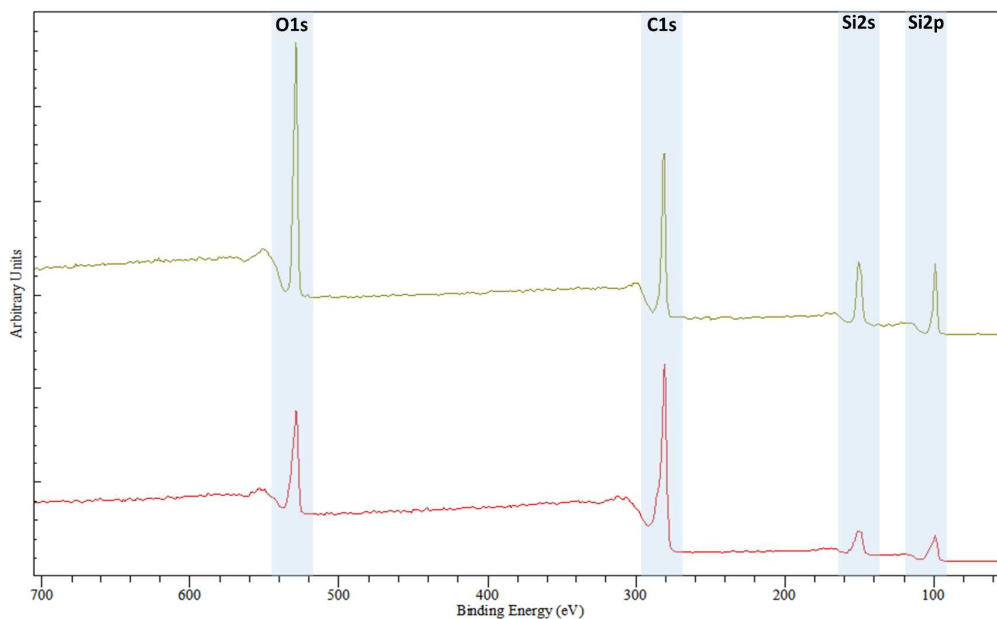
Figure 7 XPS wide scan spectra of PDMS (green) and PDMS-MWNTS sponges (red)

Mechanical properties of PDMS-MWNTs sponges

PDMS is known to be a material with excellent compressive properties both in bulk and porous form.[17] Carbon nanotubes also display superlative mechanical properties and they can strengthen polymers if used as reinforcing filler.[27–29]

Figure 8 a evidences as the stress of PDMS-MWNTs sponges at 60% strain increases with respect the PDMS alone, increasing the amount of MWNTs. In particular PDMS sponges prepared in absence of MWNTs (red curve) reach stress of 0.03 MPa at 60% strain in good agreement with previously reported results.[17] The stress increases to 0.15 MPa at 60% strain for the sample prepared in presence of 1% w/w of MWNTs (green curve) and up to 0.33 MPa at 60% strain for the sample prepared with 3% w/w of MWNTs (blue curve).
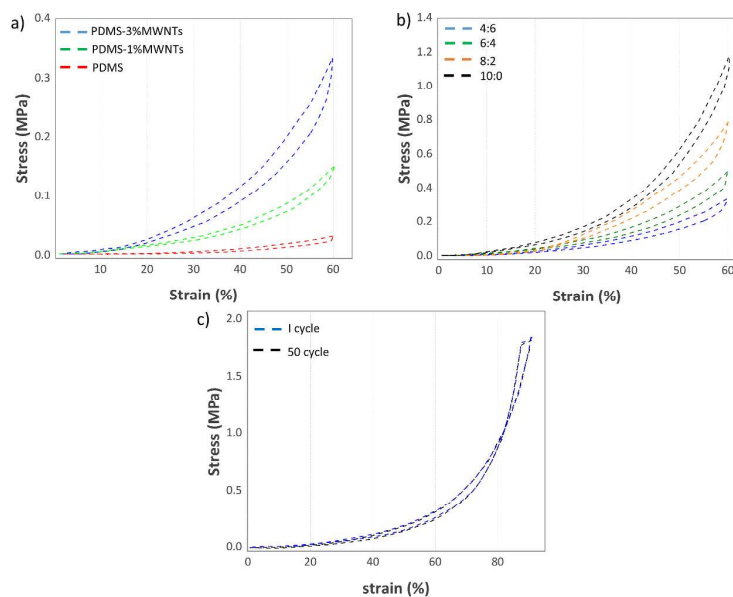
Figure 8 Compressive stress-strain curve at 60% strain of a) PDMS (red curve), PDMS-1 %MWNTs (green curve) and PDMS-3% MWNTs (blue curve), b) PDMS-3% MWNTs at ratio of m_{PDMS}/m_{HEXANE} of 4:6 (blue curve), 6:4 (green curve), 8:2 (red curve), 10:0 (black curve); c) compressive stress-strain curve at 90% strain after one and fifty cycles at ratio of m_{PDMS}/m_{HEXANE} of 4:6. In all the cases the size of GMps is 620±100 μm.

The stress of the PDMS-MWNTS 3% (w/w) sponges at 60% strain evidently increases with increasing PDMS prepolymer/hexane ratio, as shown in figure 8 b, indicating that the introduction of hexane dilutes the PDMS prepolymer and the curing agent, which leads to a decrease of the mechanical strength. Nevertheless, it should be pointed out that the value of 0.33 MPa at 60% strain for the sponge with higher dichloromethane uptake (m_{PDMS}/m_{HEXANE} of 4:6), is appropriate for oil removing applications and it is much higher than that reported for other oil-uptake systems such as metallic MWNTs sponges (66 kPa),[15] carbon aerogels (0.3 kPa),[30] 3D graphene framework (4 kPa),[31] and PDMS (12 kPa).[17]

Another important aspect is that there is not any significant change in the compressive stress-strain even after 50 cycles at 90% strain, for which a stress of 1.8 MPa was still observed (figure 8 c). Interestingly, the materials did not show any fracture or collapse during the mechanical tests confirming their high mechanical stability, which makes these sponges suitable for repeated use and recycling. The hysteresis loops indicate substantial energy dissipation due to the viscoelastic nature of the rubbery PDMS and to the expulsion of air from the open pore structure of the sponges.[32]

Wettability and stability of PDMS-MWNTs sponges

PDMS-MWNTs sponges hydrophobicity was evaluated by contact angle measurements (CA). In particular, PDMS-3% MWNTs sponges evidenced superhydrophobic behavior with CAwater ~ 153.4±6.9° (fig. 9 c), much higher than that observed on PDMS alone prepared in the same condition (CAwater ~ 131.4±6.5°, fig. 9 a) and PDMS-1% MWNTs porous nanocomposite (CAwater ~ 146.6±4.6°, fig. 9 b). This could be due to the presence of MWNTs on pore surface and/or to the increased roughness of the PDMS-MWNTs surface with respect to PDMS alone. Thanks to lightweight, porous structure and superhydrophobic properties, PDMS-MWNTs sponges can float on the surface of water. Once immersed in water by external force, it is possible to observe as the sponge is surrounded by an air cushion that allows maintaining the sponge dried after immersion (figure 9 d).
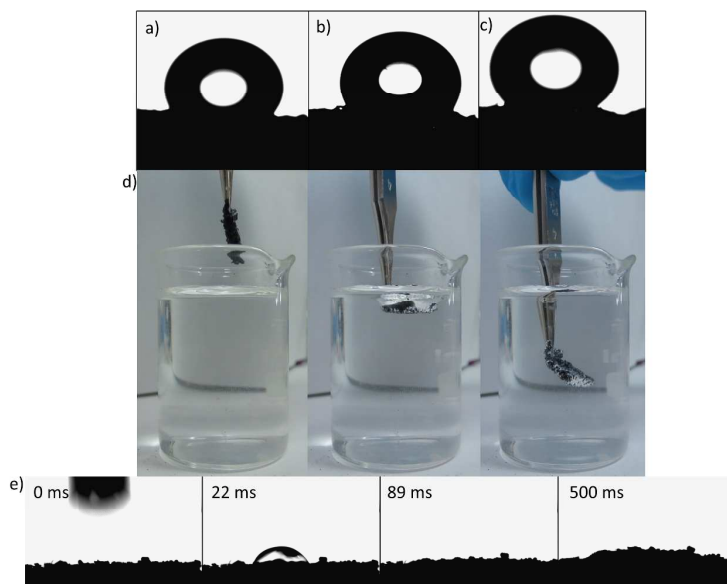
Figure 9 Optical images of a drop of water deposited on a) PDMS, b) PDMS-1% MWNTs, and c) PDMS-3%MWNTs sponges. d) PDMS-3% MWNTs sponge during immersion in water. e) time lapse of dichloromethane absorption for PDMS-MWNTs 3% w/w sponge (size of GMps is 620±100 μm)

The sponge exhibited also superoleophilic properties (CA$_{OIL}$ ~ 0°) being capable to adsorb 10 μL of oil in less than 90 ms, more than two times faster than other PDMS based porous materials.[17] Interestingly, the sponges increased their volume during the absorption process, indicating the occurrence of swelling process due to oil absorption (figure 9 d, movie S1). All these characteristics clearly evidence the superhydrophobic/superoleophilic properties and selective oil absorption capabilities of the sponge. Their superhydrophobic/superoleophilic properties could be due to a

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combined effect involving the methyl groups of PDMS and MWNTs. The former can act decreasing surface energy being on the rough surface of the sponge, the latter can further enhance this effect, being on PDMS surface and increasing surface roughness of the sponge (as revealed by SEM images, fig. 4).

Superhydrophobicity of the PDMS-MWNTs sponge is maintained also towards corrosive aqueous liquids including 1M HCl (CAwater ~ 153°) and 1M NaOH (CAwater ~ 158°).

Remarkably, the presence of MWNTs has a significant effect also in improving sponges stability, as shown in figure 10, which reports the comparison between TGA curves of the PDMS-3% MWNTs and PDMS alone sponges (blue and red curve, respectively). The presence of MWNTs increases the thermal stability of about 110°C, being detected no weight loss at temperature below ~300 °C for PDMS-3% MWNTs sponge and below ~190 °C for PDMS alone.
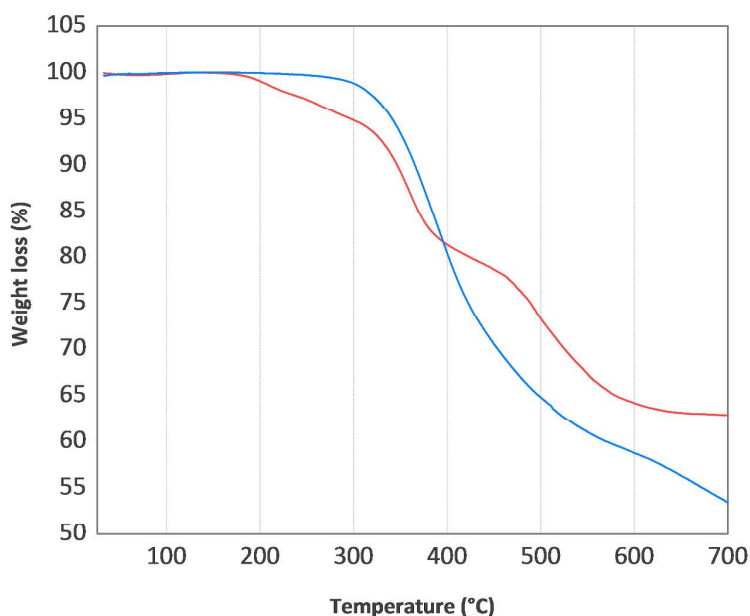
Figure 10 TGA profiles for PDMS (red curve) and PDMS-3% MWNTs (blue curve) (size of GMps is 620±100 μm).

Application of PDMS-MWNTs sponges in selective oil absorption

The verified superhydrophobic/superoleophilic properties of PDMS-MWNTs sponges as well as their 3D structure with interconnected pores certainly prompt their application in oil/water separation and oil absorption processes. Figure 11 a (movie S2) shows the ability of PDMS-MWNTs sponges to selectively adsorb oils from water surface. The floating oil could be adsorbed

in a short time, the porous structure allowing the storage of the collected oil inside the 3D structure of the sponge. As shown in figure 11 a (movie S2), besides their ideal wetting properties and oil absorption capacity, PDMS-MWNTs sponges can also be magnetically actuated in order to be driven with minimum friction onto polluted water area by means of a magnetic field. After oil absorption, no evidence of MWNTs was noticed on the surface of water indicating the good stability of the material. PDMS-MWNTs is also able to adsorb heavy oils under water if driven by an external force (fig. 11 b, movie S3).
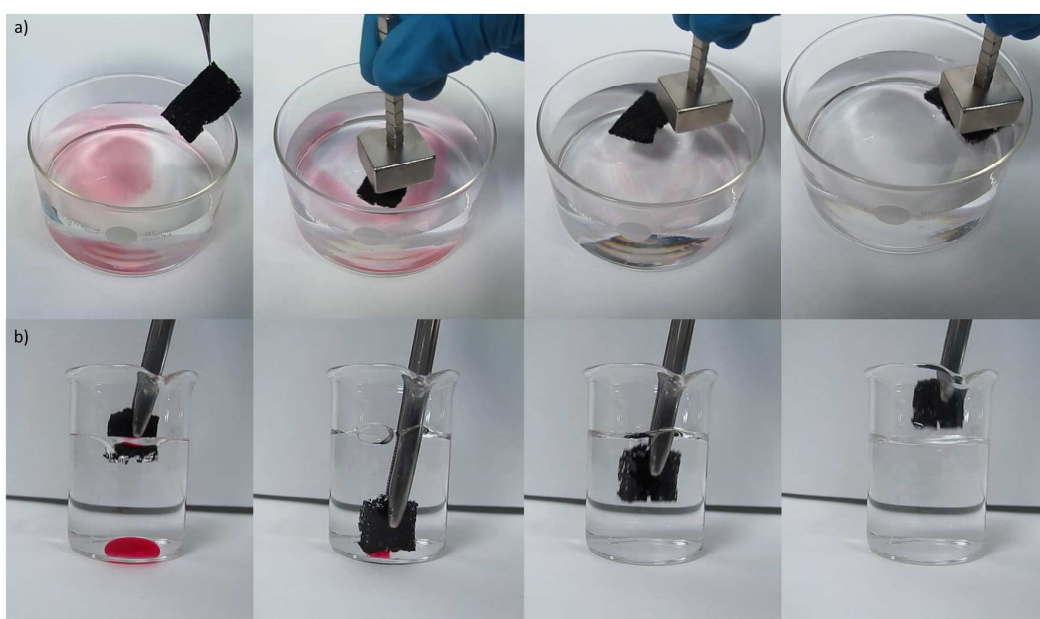
Figure 11 Removal of a) oil red O colored hexane on water surface and b) oil red O colored chloroform with PDMS-3% MWNTS (size of GMps is 620±100 μm).

PDMS-MWNTs sponges absorption capacity was tested against different oils and organic solvents. As illustrated in figure 12, changing the oil type the absorbency of PDMS-MWNTs sponge is in the range of 850% to 2000% depending on density, viscosity and surface tension of the organics.

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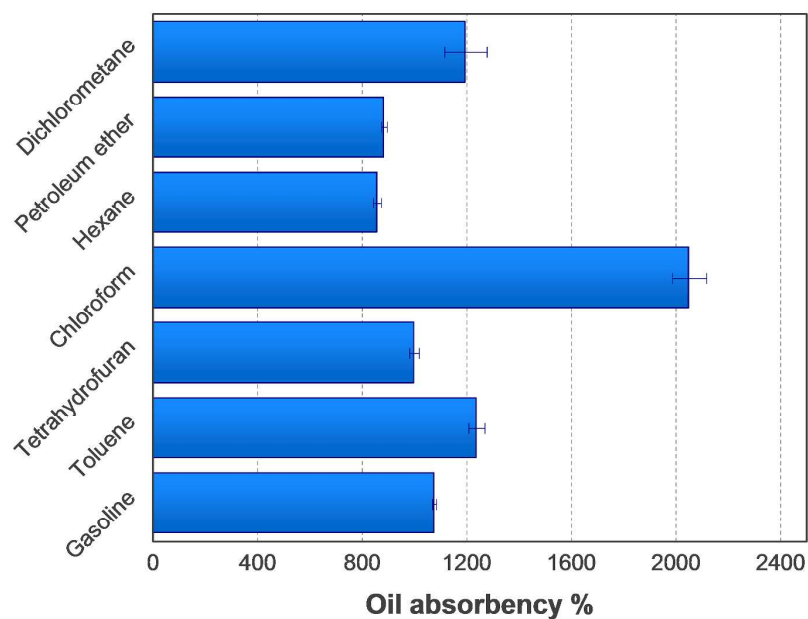**Figure 12** Different oils uptake of PDMS-3% MWNTs sponge (size of GMps is 620±100 μm)

A key point in practical oil cleanup application is the recyclability of the material and the recoverability of oil. After the uptake, the oils are stored in the large pores of the sponges and can be easily recovered by simple squeezing, as shown in figure 13 (movie S4) for chloroform as an example. To test the recyclability, PDMS-MWNTs sponges with different adsorbed solvents were squeezed and dried for 10 times and their weight was measured before and after drying. The results are summarized in table 1, where it is interesting to observe that there is no significant variation for dried and wet weight of the sponges after each cycle, independently from the solvent used for the uptake. Also water contact angle remains the same after ten cycles, suggesting that the characteristics of the material were not altered during the repeated tests.
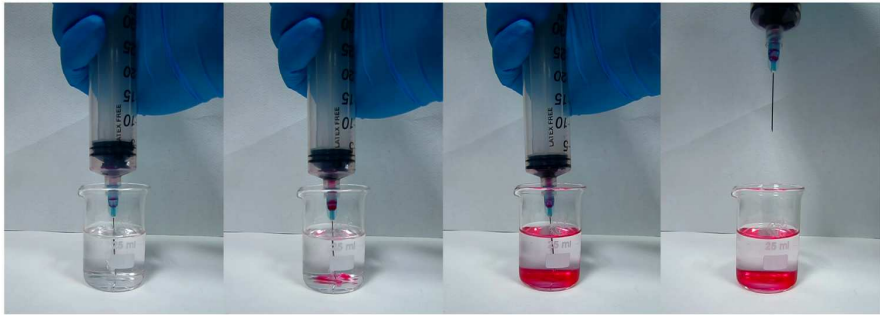
Figure 13 Recovery of adsorbed oil from PDMS- 3% MWNTs sponge by squeezing (the colorless solvent is ethanol the red one is oil red O colored chloroform).

Solvent	Cycle I		Cycle V		Cycle X	
	Dried weight %	Wet weight %	Dried weight %	Wet weight %	Dried weight %	Wet weight %
Dichloromethane	100	1031	101	1200	99	1190
Petroleum ether	100	866	101	896	100	884
Hexane	100	838	100	835	101	877
Chloroform	100	2020	100	2057	100	2080
Tetrahydrofuran	100	980	100	1022	100	1014
Toluene	100	1256	100	1231	99	1250
Diesel Oil	100	1084	99	1074	100	1089

Table 1 Dried and wet weight of PDMS-3% MWNTs for different oils after 1, 5 and 10 cycles.

Conclusion

In this study a new functional nanocomposite material based on PDMS and MWNTs is developed and its water/oil separation and oil absorption properties are demonstrated. In particular a 3D PDMS porous structure embedding magnetic MWNTs was fabricated by polymerizing PDMS prepolymer in the presence of an hard template covered with magnetic MWNTs. The proposed fabrication technique is simple and easy to be scaled up and the obtained materials are reusable. It was demonstrated that the presence of MWNTs in polymer matrices, here proposed for the first time as a way for preparing magnetic porous absorbent nanocomposites, not only provides magnetic properties to the sponges, but has also a great impact in improving their mechanical properties, thermal stability and oil uptake ability. The sponges exhibited excellent mechanical performance with respect to PDMS alone and to other proposed oil-uptake systems for which a stress at least 10 times lower at 60% strain was observed, as well as higher superhydrophobicity/superoleophilicity allowing two times faster oil sorption with respect other PDMS based porous materials. It is worth mentioning that the magnetic properties of the developed materials can be exploited in order to drive the water-repellent, oil adsorbing sponge to the polluted areas adopting non-contact methods. Furthermore after collection of organics the sponge can be driven back to recover spilled oil by simply squeezing it. The PDMS-MWNTS exhibited also high chemical and thermal stability. All these characteristics make the developed materials very attractive for real applications in environment remediation procedures.

Methods

Chemicals

PDMS prepolymer (Sylgard 184) and curing agent were purchased from Dow Corning. Magnetic MWNTs (10-15 nm in diameters, 1-10 micrometer length) were provided by Nanoledge Inc. Hexane, dichloromethane, chloroform, toluene, tetrahydrofuran, petroleum ether, ether, glucose, were purchased form Sigma Aldrich and used as received. Gasoline was purchased from Kuwait Petroleum Corporation.

Preparation of PDMS-MWNTs sponges

Porous magnetic PDMS-MWNTs sponges were prepared according to the following procedure. MWNTs were mixed overnight with 1 g of glucose particles (GMps) with size ranging from 68±29

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up to 620±100 in dry conditions at room temperature. The mixture was then packed in a syringe tube equipped with a porous septum. PDMS prepolymer and the thermal curing agent in a ratio of 10:1 by weight were placed into a glass dish and were diluted with an appropriate amount of different solvents. After being intensively stirred for 5 minutes, 10 mL of the mixture were poured in the syringe tube and infiltrated into the sugar templates with the help of a piston. The as-obtained composite was then cured in an oven at 80 °C overnight to accomplish the polymerization. The cured samples were placed in a beaker with distilled boiling water for 24 hours to dissolve the GMps and then sonicated with warm water and ethanol to remove residual sugar microparticles and not entrapped MWNTs. Different PDMS-MWNTs sponges were prepared by changing different parameters such as concentration of the prepolymer, solvent to dilute prepolymer, hard template average size, amount of MWNTs. If not differently indicated, results discussed below are referred to sponges prepared diluting PDMS pre-polymer in hexane with a ratio equal to 4:6, with hard template average size equal to 620±100 μm, with 3% (w/w) of MWNTs with respect to the template and after a contact time with oil solution of 20 minutes.

Oil absorbency and reusability of PDMS-MWNTs sponges

A piece of sample was immersed in oil bath at room temperature for 20 minutes. After that, the sample was removed from oil, wiped with filter paper in order to remove excess oil and weighed. The oil mass sorption capacity (absorbency) was evaluated as $(m-m_0)/m_0 \times 100\%$, where m is the weight of the sample after sorption and m_0 is the initial weight of the sample. Repeated absorption-desorption cycles of oils were performed to evaluate sponge reusability. For this purpose, the sample was immersed in oil until absorption equilibrium was reached (i.e. 20 min), and then weighted to calculate the sorption capacity. The sample was then squeezed and washed with ethanol for three times and dried in an oven at 60 °C. The absorption-desorption procedure was repeated 10 times for each tested oil.

Characterization of the PDMS-MWNTs sponges

The dynamic and static contact angle measurements were carried out using the OCA 15 Plus instrument (DataPhysics Instruments, Filderstadt, Germany), equipped with a high-resolution camera, with an automated liquid dispenser. SCA 20 software was employed to obtain additional information on the samples: the software uses the algorithm based on the Young-Laplace equation and it allows to correlate the shape of the drop with its surface tension and to measure the contact angle between the liquid and the analyzed surface.

XPS measurements were performed with an AXIS ULTRA DLD (Kratos Analytical) electron spectrometer using mono Al Kα source (1486.6 eV) operated at 225 W (15 kV, 15 mA). Survey scan spectra were recorded using pass energy of 160 eV and a 1 eV step. Narrow scans of single regions were acquired using a pass energy of 20 eV and a 0.1 eV step. The hybrid lens mode was used for all measurements. In each case the area of analysis was about 700*300 μm. Base pressure in the analysis chamber was 2*10-9 torr. During the acquisitions a system of neutralization of the charge was used. Processing of the spectra was accomplished with CasaXPS Release 2.3.16 software.

Morphological characterization of PDMS and PDMS-MWNTs samples at the micro and nanoscale was carried out using a scanning electron microscope (SEM) JEOL JSM-6390 at an acceleration voltage of 3 kV

Quasi-static hysteresis compression tests were performed on a LLOYD LR5K dynamometer equipped with 50 mm diameter parallel plate tools and 1 KN load cell. Tests were performed by loading the samples to different strain levels, equal to 60 and 90%. The loading and the unloading stages were performed at the same rate of deformation of 2 mm/min. Each test reported was obtained as the average of three samples.

Thermogravimetric analysis (TGA) was performed on a Mettler Toledo DSC/TGA1 instrument, by heating 20 mg samples between 30 and 700 °C at 10 °C/min heating rate in nitrogen atmosphere.

Supporting information Available: Movie S1 time lapse of dichloromethane absorption for PDMS-MWNTs 3% w/w sponge (size of GMps is 620±100 μm). Movie S2 Removal of oil red O colored hexane on water surface with PDMS-3% MWNTS magnetically actuated sponge (size of GMps is 620±100 μm). Movie S3 Removal of oil red O colored chloroform with PDMS-3% MWNTS (size of GMps is 620±100 μm). Movie S4 Recovery of absorbed oil from PDMS-3% MWNTS (size of GMps is 620±100 μm)by squeezing. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to
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Figure Captions

Figure 1 a) Schematic illustration of the preparation of PDMS-MWNTs sponge; b) Photograph of PDMS-MWNTs sponge anchored to a magnet

Figure 2 Dichloromethane sorption (%) of the PDMS-MWNTs sponges with different mPDMS/mhexane (the size of GMps is 68±29μm and 3% (w/w) of MWNTs with respect to GMps is used).

Figure 3 Variation of absorbency of the PDMS/MWNTs sponges for dichloromethane with different solvents used to dilute PDMS pre-polymer (the size of GMps is 68±29 μm and 3% (w/w) of MWNTs with respect to GMps is used)

Figure 4 SEM images of porous PDMS-MWNTs with the size of GMps equal to a) 68±29 μm and b) 620±100 μm (with the relative zoom in c). d) porous PDMS with the size of GMps equal to a). Scale bar is 200 μm. e) Oil absorbency of PDMS-MWNTs sponges prepared from different templates.

Figure 5 Oil absorbency of PDMS/MWNTs sponges prepared from different ratio of MWNTs with respect to GMps

Figure 6 Oil absorbency for different contact time with PDMS-MWNTs (the size of GMps is 620±100 μm and 3% (w/w) of MWNTs with respect to GMps is used)

Figure 7 XPS wide scan spectra of PDMS (green) and PDMS-MWNTS sponges (red)

Figure 8 Compressive stress-strain curve at 60% strain of a) PDMS (red curve), PDMS-1 %MWNTs (green curve) and PDMS-3% MWNTs (blue curve), b) PDMS-3% MWNTs at ratio of mPDMS/mHEXANE of 4:6 (blue curve), 6:4 (green curve), 8:2 (red curve), 10:0 (black curve); c) compressive stress-strain curve at 90% strain after one and fifty cycles at ratio of mPDMS/mHEXANE of 4:6. In all the cases the size of GMps is 620±100 μm.

Figure 9 Optical images of a drop of water deposited on a) PDMS, b) PDMS-1% MWNTs, and c) PDMS-3%MWNTs sponges. d) PDMS-3% MWNTs sponge during immersion in water. e) time

lapse of dichloromethane absorption for PDMS-MWNTs 3% w/w sponge (size of GMps is 620±100 μm)

Figure 10 TGA profiles for PDMS (red curve) and PDMS-3% MWNTs (blue curve) (size of GMps is 620±100 μm).

Figure 11 Removal of a) oil red O colored hexane on water surface and b) oil red O colored chloroform with PDMS-3% MWNTS (size of GMps is 620±100 μm).

Figure 12 Different oils uptake of PDMS-3% MWNTs sponge (size of GMps is 620±100 μm)

Figure 13 Recovery of adsorbed oil from PDMS- 3% MWNTs sponge by squeezing (the colorless solvent is ethanol the red one is oil red O colored chloroform).

a)

Packed GMp-
MWNTs template

PDMS
prepolymer

Packed GMp-
MWNTs template
+PDMS prepolymer

1)   80°C
     /16hs

2)   Washing

PDMS-MWNTs
sponge

b)

Porous septum
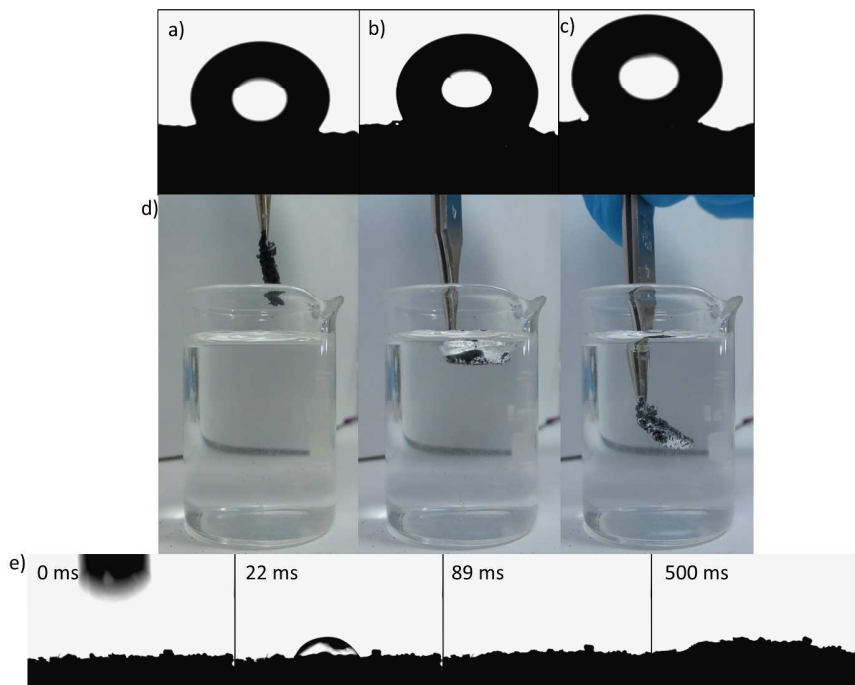
GMp-MWNTs template

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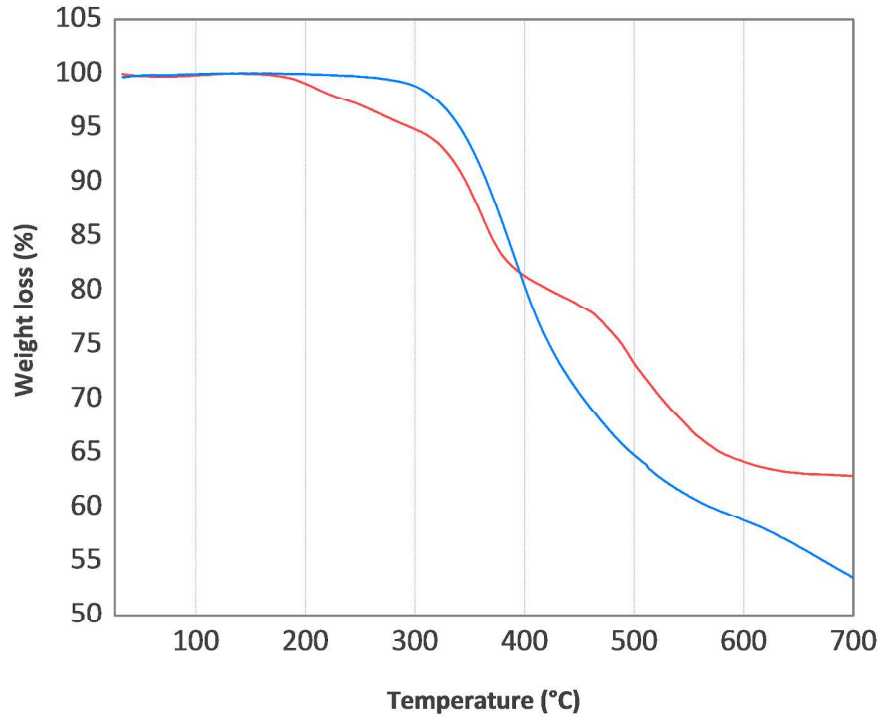46
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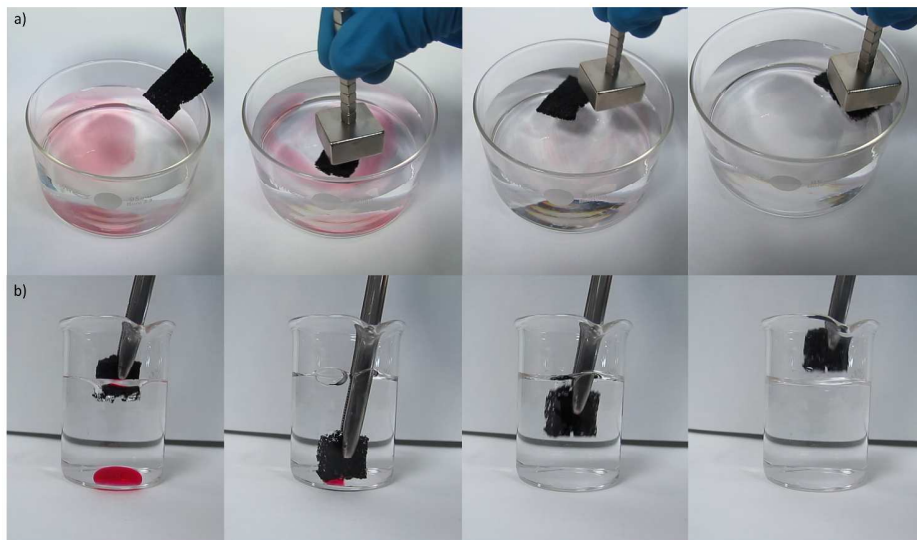51
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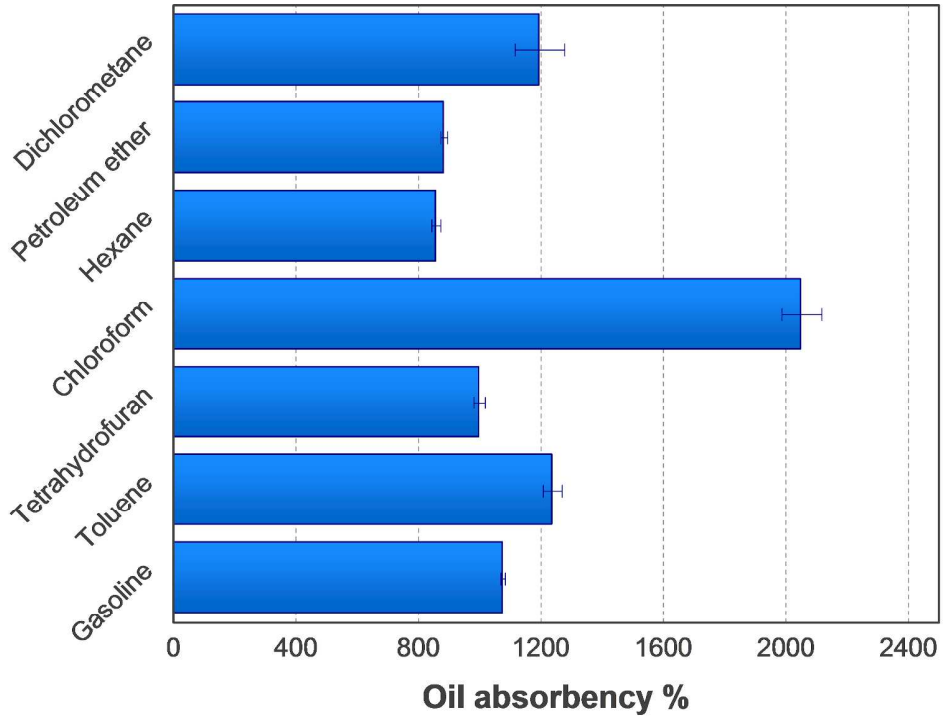48
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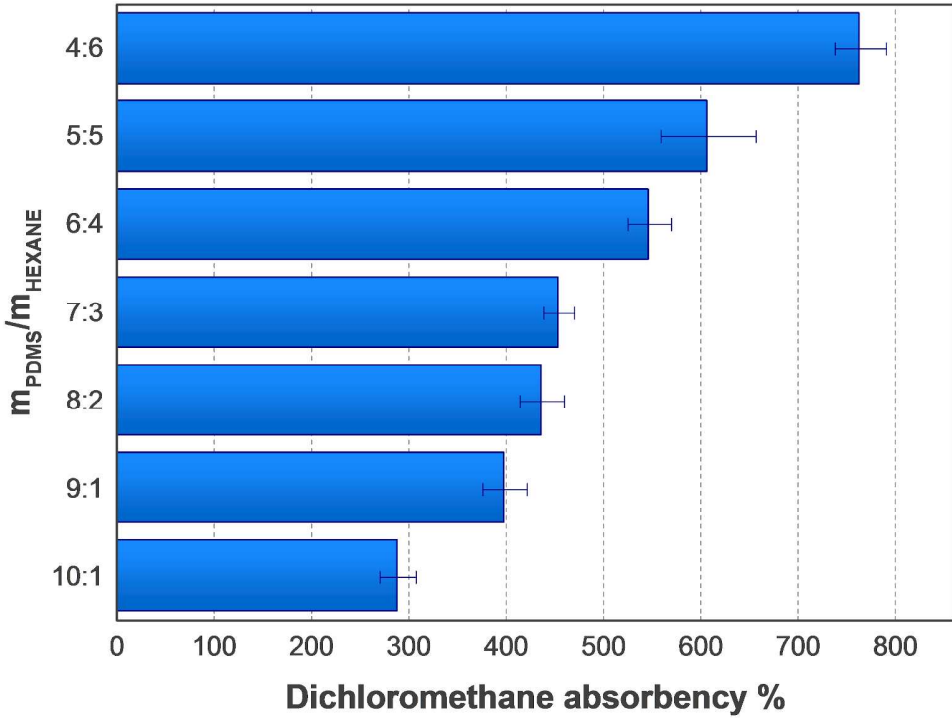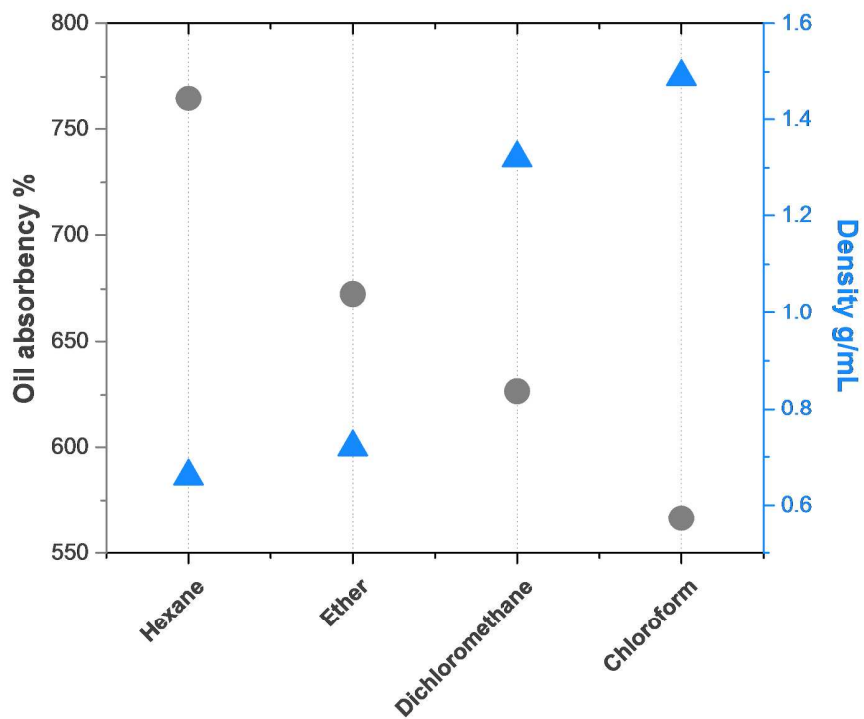
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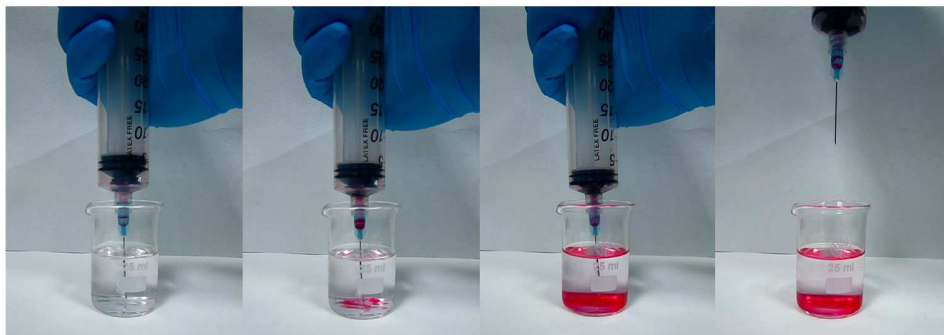

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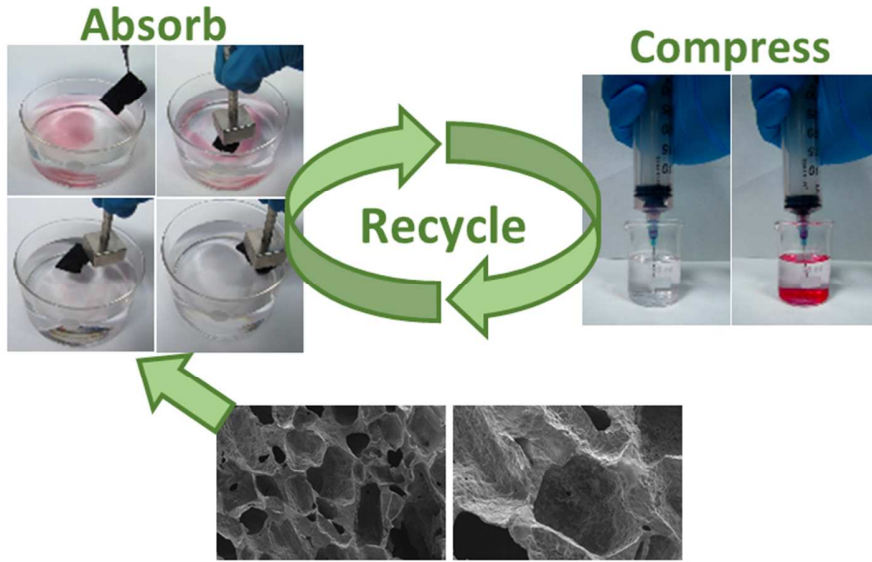45
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