

Selective Separation of Oil from Water via Superhydrophobic Magnetic Foams.

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ABSTRACT

We demonstrate an inexpensive alternative technique of magnetically actuated superhydrophobic foams. A simple, commercial polyurethane foam is used as a substrate on which a small amount of colloidal iron oxide superparamagnetic nanoparticles solution is drop casted. The subsequent deposition of polytetrafluoroethylene (PTFE) particles by a dry transfer technique allows the surface to become superhydrophobic. The presence of the iron oxide nanoparticles increases the speed of oil absorption by the functionalized foam, which due to its superhydrophobicity makes possible the oil/water separation. Moreover the samples are easily actuated by a weak magnetic field on a water oil interface driving and directing them to the oil polluted area. A detailed microscopy and wettability study reveals the characteristics of the presented systems explaining thus the mechanism of the nanoparticles/ PTFE assembly and their superhydrophobic/superoleophilic properties.

Keywords: hydrophobicity, oleophilicity, foams, magnetic actuation, water/oil separation

1 INTRODUCTION

Nowadays, due to the increased attention to the environmental protection, the scientific community is showing a growing interest for the formation of new materials able to capture and remove various forms of organic contaminants or oil spills from water. For this scope, diverse studies have been conducted, showing though various limitations, with one of the most important their unsuitable wetting behavior [1, 2]. Practically, various systems present coadsorption of water and oil guiding to the lack of substantial selectivity or to the low separation efficiency of these materials. In order to avoid this drawback, it is necessary the formation of materials with superhydrophobic/superoleophilic properties. Specifically, since the surface tension of the water is much larger than that of the oil, if the surface tension of a solid substrate lies between those of water and oil, it might show simultaneously hydrophobicity and oleophilicity. Thus, the oil can easily wet and penetrate many superhydrophobic

surfaces. Combined with an appropriate surface design, there are prepared surfaces that exhibit superhydrophobicity and superoleophilicity capable to separate oil from water mixtures [3, 4, 5]. However, the fabrication process is in principle complicated and time-consuming. Recently, a facile and inexpensive technique was presented, where it is obtained water/oil separation by using simple filter paper coated with particles [6]. This technique is very promising but the lack of actuation of this membrane by an external stimulus in order to direct it at the desired polluted area may be a limit for its wide applicability.

Here we demonstrate an alternative technique which is also inexpensive and very facile, but above all, it presents an extra very important parameter, which is the magnetic actuation of the developed filter. In particular, a commercial polyurethane foam is used as a substrate on which a small amount of toluene solution containing colloidal iron oxide superparamagnetic nanoparticles is drop casted. Subsequently, PTFE particles were deposited on the surface by a dry transfer technique. Although it is reported that the specific particles are sufficiently oleophilic and are widely used for the water oil separation, [7, 3] the addition of iron oxide nanoparticles below the PTFE layer on the presented system increases dramatically the rate of oil absorption. Moreover the samples are easily actuated by a weak magnetic field on a water oil interface driving and directing them to the oil polluted area. This is a very promising technique, since these materials might be applied to the fast and selective cleanup of large-area oil spills by driving the filters by distance with simple application of magnetic fields saving thus energy and moreover with increased absorption efficiency.

2 EXPERIMENTAL METHODS

2.1 Materials

The polyurethane VITA cellular foams are purchased by (VITEC, Inc, UK). Nearly spherical mixed-phase nanocrystals of γ -Fe₂O₃/Fe₃O₄ of 10 nm diameter were synthesized by a wet-chemical synthetic approach. Briefly, iron pentacarbonyl (Fe(CO)₅, Aldrich 97%) was used as the precursor which was decomposed at 320°C under inert atmosphere, in the presence of 1-octadecene (ODE, Aldrich

90%) and of oleic acid (OLAC, Aldrich 90%), as both capping molecules and reactivity moderators. Size control was achieved by varying the concentration of the precursor and the surfactant-to-precursor molar ratio. Detailed studies showed that the principal capping molecule of the synthesized nanoparticles is the OLAC. PTFE particles of diameter 150-200nm (Aldrich) were used as is. All solvents used were purchased by Aldrich.

2.2 Samples Preparation

Foams substrates of dimensions $2 \times 1.5 \text{ cm}^2$ were first washed in cyclopentanone upon dipping, for three times, and dried carefully under nitrogen flow. Four types of samples were prepared: At the first one, PTFE particles were applied on the surface of the cleaned foams by a dry transfer technique at a weight percentage of 40% with respect to the weight of the foam (from now on named T); at the second type on the T samples was drop casted a toluene solution containing 3.5mg of NPs, (named as TNP); at the third one on a clean foam was drop casted toluene solution containing 3.5mg of nanoparticles (named as NP); and at the fourth type on a NP sample PTFE particles were deposited, by the dry transfer technique, with the same weight percentage as at the sample T (named NPT). The dry transfer technique takes advantage the electrostatic interaction between the substrate and the particles which are highly activated by the friction, guiding thus to the assembly of the particles on the substrates surface.

2.3 Samples Characterization

Measurements of the wetting properties were carried out with a KSVCAM200 instrument. The microscopy study was conducted with an optical microscope (Carl Zeiss, Axio Scope A1) equipped with a digital camera and image processing software.

3 RESULTS AND DISCUSSION

The morphology of the samples formed was firstly investigated with optical microscopy (Figure 1). Figure 1a demonstrates the bare foam (sample F) which has a smooth surface. This is the case also for the NP sample, since features in the nanoscale is impossible to be observed with this type of study (image not shown). On the other hand, at the surface of the T, NPT and TNP samples it is evident the existence of aggregated structures corresponding to the PTFE particles. Particularly the T surface contains highly concentrated big agglomerates of particles, which is not the case at the other two types of samples, where the particles are much better dispersed forming small aggregates well distributed all around the foam fibers. These aggregates increase the roughness of the surface compared to the bare foam and to the NP sample.

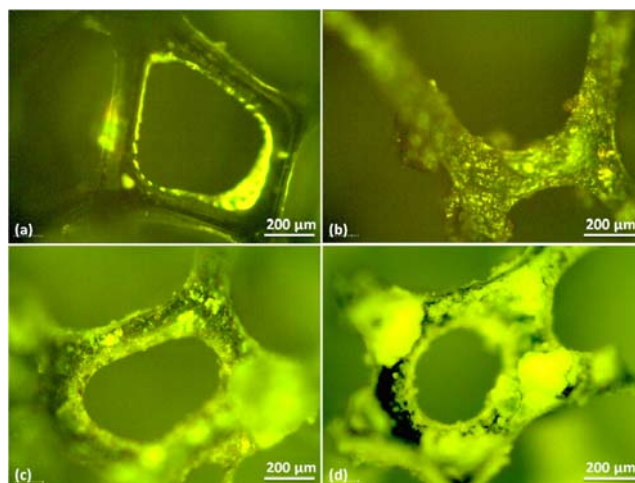


Figure 1. Microscope images of F (a), TNP sample (b), NPT (c) and T (d).

This type of roughness affects the wetting properties of the samples as shown at Figure 2. In particular, the static water contact angle (WCA) of the foam which is ca. 115° increases after the application of the nanoparticles (sample NP), due to the existence of the hydrophobic capping molecules around the iron oxide. When on the foam are applied PTFE particles, the sample becomes superhydrophobic and self cleaning as shown by both the WCA and the hysteresis measurement (WCA higher than 150° and hysteresis less than 10° [8]). The same behavior is observed when the PTFE is applied on the top of the NP sample (sample NPT). This indicates that when the PTFE is the last layer, the whole material becomes superhydrophobic and self cleaning. However, when above the PTFE layer is casted the nanoparticle solution, the superhydrophobicity is lost, while the hysteresis is highly increased, indicating that the colloidal nanoparticles affect the properties of the PTFE surface after wetting it.

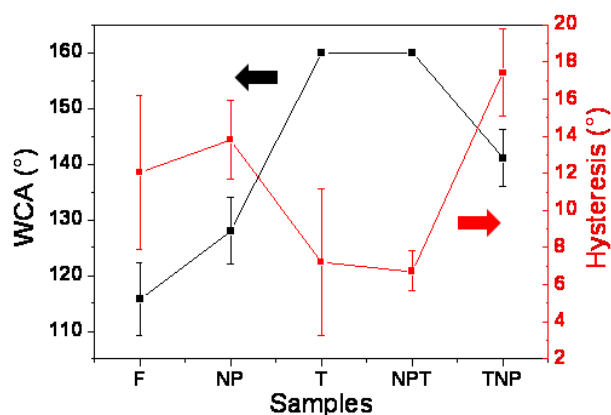


Figure 2. Water contact angle (WCA) and hysteresis measurements, conducted to all the prepared samples.

In order to examine the oleophilic properties of the samples, instead of water it was placed an oil drop on each of them. Initially the examined foam is oleophobic with oil

contact angle (OLA) of $87.46^{\circ} \pm 8.72^{\circ}$. This is not the case to the rest of the samples, where the oil is absorbed. As already mentioned the PTFE particles are oleophilic and are industrially used for the water oil separation. However when a layer of iron oxide nanoparticles is applied below the PTFE layer as done at the NPT sample, the oil droplet is absorbed 2.6 times faster compared to the T sample (Figure 3a). By measuring the reduction of the volume of the oil droplet during time it is possible to calculate (by the slope of Fig.3a) the speed of the oil absorption. Particularly as shown at Figure 3b, the initially oleophobic foam becomes oleophilic and oil absorbing after the treatment with both PTFE particles and iron oxide nanoparticles. Nevertheless, the speed of the absorption is different. When nanoparticles are deposited on the top of the foam, it becomes oleophilic, with absorption speed ca. $13 \mu\text{l/s}$. This speed is 2.3 times higher compared to the T sample, indicating that the nanoparticles are much more oleophilic than the PTFE particles. The combination of particles (NPT sample) increases even more the absorption rate, which is now 2.6 times higher compared to the T, while at the TNP sample the change is not significant compared to the NP. These results designate that the colloidal iron oxide nanoparticles are responsible for the high efficiency of the oil absorption, due to both their oleophilic character but also due to the oleophilic character of the oleic acid which is the main capping molecule of the nanoparticles.

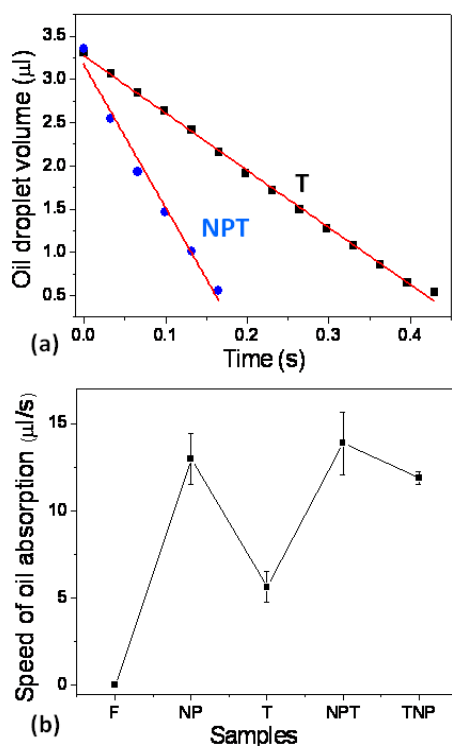


Figure 3. (a) Volume change of an oil droplet deposited on a T or NPT sample during time. (b) Calculated speed of the oil absorption for all the presented samples. (The initial droplet volume was $3.5 \mu\text{l}$ in all cases).

Although the oil absorption speed is similar in all three samples (NP, TNP and NPT), as already shown at Figure 2 the wetting properties are completely different. Among these, the NPT sample is the only one superhydrophobic and water repellent. Thus, the NPT sample combines perfectly the desired superhydrophobic, and self cleaning properties and the highly efficient oil absorption properties. This combination makes the NPT sample a promising candidate for the use in the water oil separation. In fact Figure 4 shows how oil is separated by a drop containing both water and oil. In particular the initial symmetrical drop (Fig. 4a) of both substances is phase separating (Fig. 4b), and the oil part is absorbed leaving the water on the surface (Fig.4c).



Figure 4. Images of the sequence of oil separation from a drop of oil/water mixture.

Moreover the existence of the magnetic nanoparticles makes the modified foam magnetic, easily actuated by an external field. Figure 5 demonstrates the NPT sample, placed on a water container with oil drops, which is easily actuated and driven to the oil polluted area by a magnetic field of about 100mT.

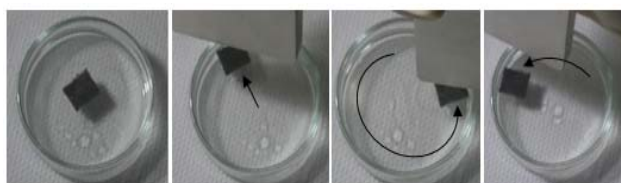


Figure 5. Magnetic actuation of an NPT sample on a water container with oil drops. The arrows show the movement of the magnet and consequently of the sample.

4 CONCLUSIONS

We have demonstrated an alternative, inexpensive and very facile technique for removing oil from water in an effective way, using magnetically actuated functionalized polyurethane foams. Iron oxide colloidal nanoparticles are deposited on the oleophobic foams and the subsequent deposition of PTFE particles makes the material superhydrophobic and oil absorbing. The speed of absorption is remarkably increased compared to samples functionalized only with PTFE. In addition, the samples can be magnetically actuated, thus they can be driven and directed to the oil polluted areas. This is a very promising technique since these materials might be applied to the fast and selective cleanup of large-area oil spills by driving the filters by distance with simple application of magnetic fields saving thus energy and moreover with increased adsorption efficiency.

Track: Advanced Materials
Topic: Nanostructured Coatings, Surfaces & Films:
Superhydrophobic/hydrophilic surface applications

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