Magnetically Induced Drop Movement on Nanorough Micropatterned Nanocomposites

Athanasios Milionis[1], Despina Fragouli[1], Ilker Bayer[1], George C. Anyfantis[1] , Roberto Cingolani[2], Athanassia Athanassiou[12]

1 Center for Biomolecular Nanotechnologies @UNILE, Istituto Italiano di Tecnologia (IIT), Via Barsanti, 73010 Arnesano, Lecce, Italy
2 Istituto Italiano di Tecnologia (IIT), Via Morego 30, 16163, Genova, Italy

ABSTRACT

Here is presented a study of smart solid superhydrophobic magnetic surfaces, which show tunable wetting behavior by varying the geometrical arrangement of the surface roughness, and by applying an external magnetic field. In particular, hybrid organic/inorganic rough surfaces were developed by exploiting photo-lithographically tailored patterns of SU-8 polymer nanocomposites containing a small amount of colloidal nanoparticles of iron oxide, either mixed directly in the polymer matrix or casted on the surface by a spraying technique. The role of the nanoparticles has two aspects. The first one is to induce surface nanoscale roughness which can be enhanced upon their vertical alignment inside the matrix, and the second one is that after the UV photopatterning the resulting pillars are able to move upon the application of an external magnetic field. The resulting nanocomposite patterns exhibit higher hydrophobicity compared to the same pillars formed only with the SU-8. Moreover the actuation of these structures by the external magnetic field is able to drive the movement of water drops deposited on them towards specific directions. For the further modification of these smart surfaces it is applied on the final surface a coating of superhydrophobic polytetrafluoroethylene (PTFE) particles with the spraying technique, enhancing thus the already existing roughness. This results in the increase of the superhydrophobicity of the nanomposite system, giving thus the possibility for easier drop movement.
.

Keywords: Superhydrophobicity, Micropatterning, Magnetic actuation, Nanoroughness, Drop Movement

1 INTRODUCTION

The fabrication of functional surfaces with controlled wetting properties, which can respond to external stimuli, is of great research interest, due to their wide range of potential applications, including microfluidic devices, controllable drug delivery, and self cleaning surfaces. Due to the fact that wetting properties of materials are governed by the joint effects of their inherent chemical nature and surface geometrical arrangement, tailored surfaces that exhibit specific wetting characteristics can be obtained by appropriate compositional and structural engineering. Indeed, recent studies have shown that the combination of patterned substrates with appropriate materials exhibit a tunable wetting behavior under external stimuli [1]-[4].

In this work we demonstrate the possibility to tailor the wettability characteristics of patterned surfaces created with a photosensitive nanocomposite resin. This nanocomposite resin contains superparamagnetic nanoparticles able to respond to an external magnetic stimulus. On the surface of the specific patterns they may be added further coatings of magnetic nanoparticles, enhancing thus both the magnetic actuation possibility and the nanoroughness, or PTFE particles which increase dramatically the hydrophobicity and decrease the hysteresis of the patterns. This process makes possible the spontaneous movement of a water drop placed on the top of the modified pillars by the application of a weak magnetic field.

2 MATERIALS AND METHODS

SU-8 is a commercial biocompatible epoxy-based negative photoresist that is suitable for the microfabrication of high aspect-ratio (>20) structures [3]. It absorbs at the UV range of the spectrum with a maximum efficiency at 365 nm. When exposed, the SU-8's molecular chains crosslink causing the polymerization of the material. Here it was used the SU-8 3050 purchased from Microchem. The process followed for the fabrication of the SU-8 pillars involves the steps of spin-coating on a silicon wafer, soft-bake, UV exposure with mask-aligner, post-bake and development as they are provided by the datasheets of the company [5]. A mask of square shaped pillar patterns was used with 42 μm side with different interpillar distances varying from 14-77 μm.

Iron oxide colloidal nanoparticles of diameter 20 nm in choloroform solution, were synthesized by a wet-chemical synthetic approach. Briefly iron pentacarbonyl was used as precursor and decomposed in a hot non coordinating solvent in the presence of a long-chain carboxylic acid under inert atmosphere. Size control was achieved by varying the concentration of the precursor and the surfactant-to-precursor molar ratio.

PTFE particles from Sigma Alldrich (1 μm) were dispersed in acetone or chloroform solution by sonication for a couple of minutes until it was obtained a homogeneous solution. Subsequently, a spray-coating setup, driven by a high-pressure airstream (120 kPa), is used to deposit the particles through a confined nozzle head, where the high-pressure flow breaks the suspension into miniature aerosol droplets. The distance between the sample and the nozzle head was approximately 20 cm. The concentration of the particles was varying from 1-6 % wt.

For the fabrication of the superhydrophobic magnetic patterns were used two different approaches. Initially a part of the iron oxide chloroform solution was mixed with the prepolymer solution under sonication, for homogenous dispersion. The second approach was to first create the pillars by pure SU-8 and then by the spray-coating method application on the surface of the patterns the nanoparticles.

For the direct insertion of the nanoparticles inside the SU-8 resin the procedure followed was first to evaporate the existing cyclopentanone from the SU-8 3050 resin. Consequently it was dissolved in chloroform (1:5 wt.) by sonication for 10 min and then stirring. Then iron oxide nanoparticles (2% wt.) were slowly added and mixed with the SU-8 solution under sonication. After obtaining a homogeneous solution, the solvent was slowly evaporated under nitrogen flow, until it was obtained a nanocomposite solution viscous enough to form a thick coating. The solution was then spin-coated on a silicon wafer and subsequently left under a magnetic field (400 mT) with a vertical direction with respect to the substrate, resulting in the formation of wire like magnetic structures. After, the sample was irradiated with a UV lamp mask alligner for 70 sec with energy of 25 mW. The post-bake was for 1 min at 65^{o} C and for 4 min at 95^{o} C. Finally the samples were developed with SU-8 developer (15min) and rinsed with isopropanol with subsequent drying under nitrogen flow. The fabricated nanocomposite pillars formed in this way, had a square side of 42 um and they were 40 um high (Figure 1a). Figure1b demonstrates a higher magnification SEM image, where can be recognized the magnetic wires inside the SU-8 matrix, formed due to the external magnetic field These magnetic wires induce magnetic anisotropy so for specific magnetic field orientations the magnetic response is higher [6].

An alternative approach followed was the fabrication of high-aspect ratio pure SU-8 pattern, on which it was sprayed a coatings of iron oxide nanoparticles and PTFE particles (Figure 2) The resulting patterns of pillar square arrays had an aspect-ratio 5:1, and were produced with the mask of 77 µm interpillar distance.

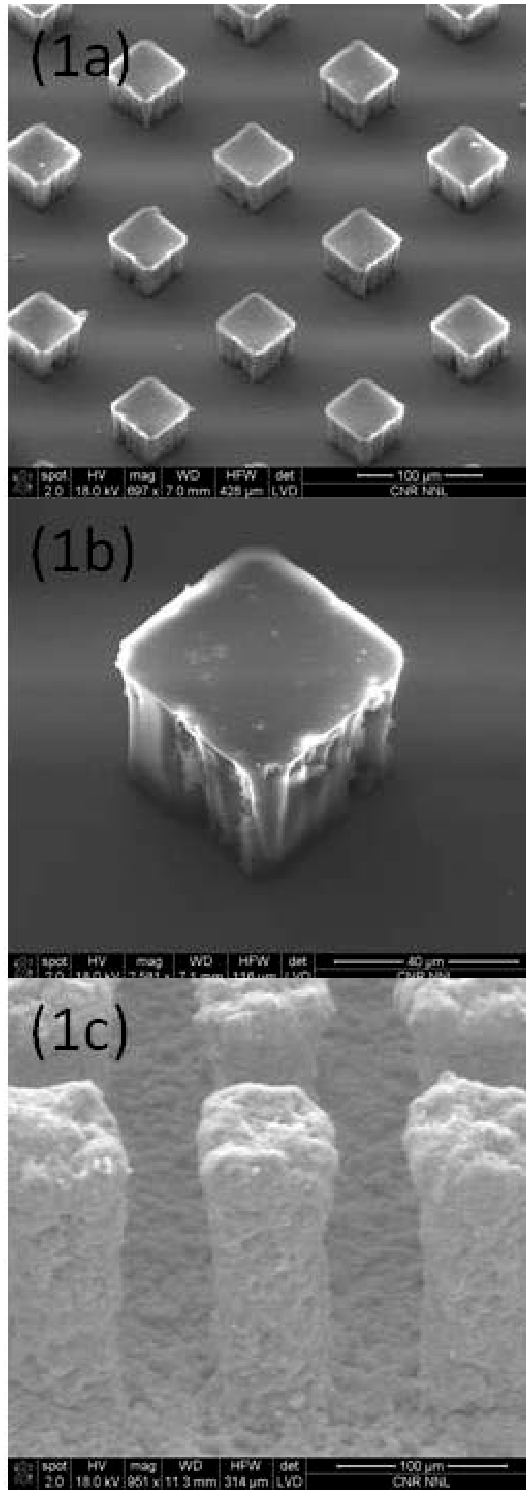


Figure 1: (a) SEM image of the SU-8/iron oxide nanocomposite pillar structures. (b) Magnification of one pillar where it is clearly seen the vertical aligned wires of the nanoparticles. (c) SEM image of the SU-8 pillars with iron oxide nanoparticles and PTFE particles spray-coated on their surface.

3 RESULTS AND DISCUSSION

The magnetic alignment of the iron oxide nanoparticles inside the SU-8 matrix creates a magnetic anisotropy that enhances the possibility for the pillar structures to respond to an external magnetic field with direction parallel to the wires. In order to achieve the water drop movement due to the magnetic actuation of the pillars, apart from the magnetic properties that the nanocomposite material should have, it is also required a superhydrophic surface with low hysteresis value. This is expected to assist the water drop to move from the surface that it is lying. For this reason, it is conducted a wettabilty characterization of the produced samples.

The water contact angle (WCA) measured for these square patterned arrays of 40 μm height nanocomposite pillars with square side 42 um and interpillar distance 14 μm is 137.41 ± 0.09^o for, while for higher interpillar distance (77μm) the WCA falls to 104.86 ± 0.15^o. These values are very close to the original SU-8 wettability values for this type of patterns. Moreover, as in the case of pure SU-8, the surface of the pattern is very sticky so that the water drop remains in contact with the surface even for inclination of 90^o.

In order to estimate if a water droplet placed on these magnetic pillars can move upon an external magnetic field, the sample was inclined so that it could be observed a difference between the right and the left part of the drop. After, a static magnet of maximum field strength 500 mT, was moving continuously back and forth, close to the sample, with a direction parallel to it. After few minutes it was observed a change in the shape of the drop when the magnet was moving towards the drop, while it was recovering when the magnet was far from the substrate, (Table 1). Although there is no drop movement, this difference in the shape of the drop possibly indicates a tendency of the drop to move.

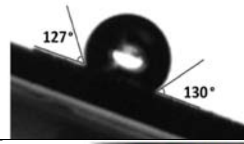
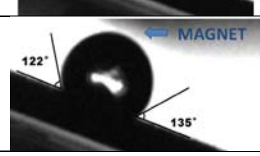
Left part	Right part	Image
127	130	
122	135	

Table 1: Contact angle values of the left and right part of the water drop when the magnet is away from the substrate (top raw) and when the magnet in coming closer. At the last column are demonstrated the two examined frames.

In order to increase the possibility for the drop movement to occur a different approach was followed that improved the system's hydrophobicity and lowered its hysteresis. Specifically, when iron oxide nanoparticles were sprayed on the top of the already fabricated SU-8 pillars, it was observed a significant increase in the WCA. The nanoparticles which remain attached to the external surface of the SU-8 matrix are able to induce very big increase in the surface roughness, as shown at the AFM image of figure 3a compared to the nanocomposite pillars without spay-coated layer of nanoparticles on the top (Fig. 3b). The WCA at this type of surface is increased by 30° compared to the aligned nanocomposite.

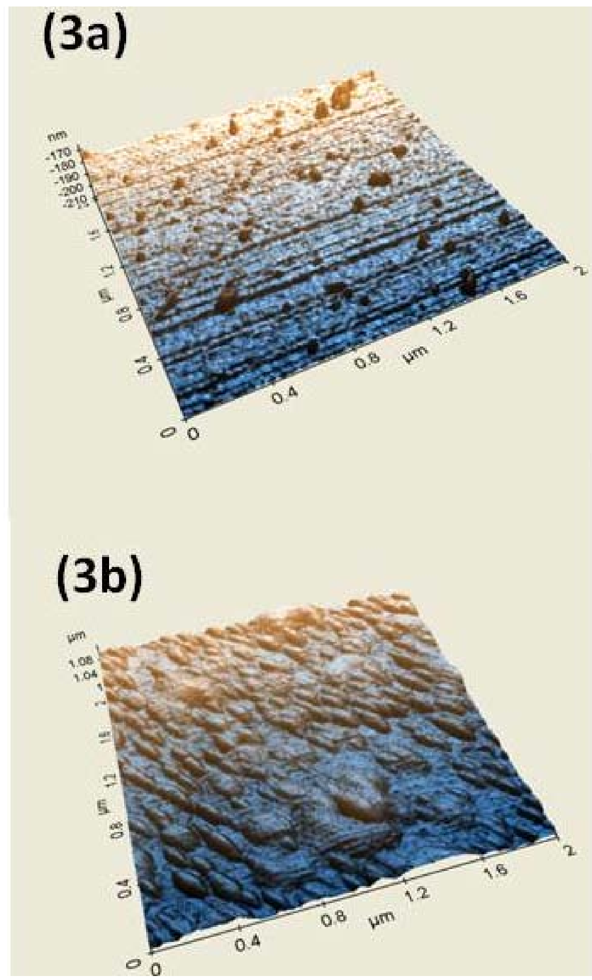


Figure 3: (a) AFM image of the SU-8 surface with spray coated iron oxide nanoparticles (28 nm mean size) (b) the topography of the nanocomposite SU-8 mixed with iron oxide, vertically aligned.

Despite the fact that these patterns become superhydrophobic the hysteresis remains very high as the drop "sticks" on the surface even while tilted 90^o. In order to eliminate this effect it was spray-coated an extra layer of PTFE particles that are known for their superhydrophobic and low hysteresis properties. The result was that the patterns became superhydrophobic having all of them WCA values above 160^o and the hysteresis values were significantly lowered below 10^o. (Fig. 4)

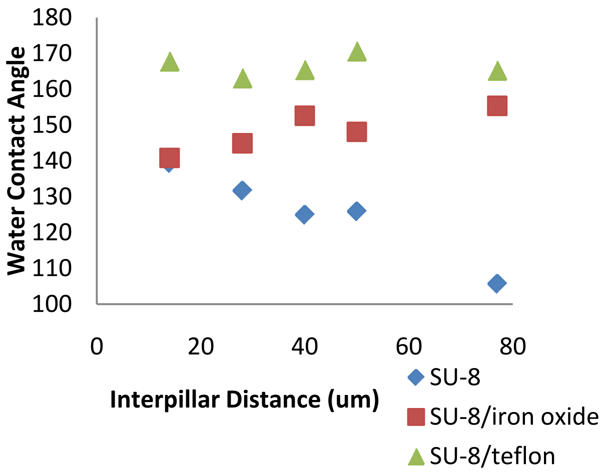


Figure 4: WCA values for the SU-8 pillars, SU-8 pillars with the coating of Fe_2O_3 nanoparticles and SU-8 pillars with the PTFE particles. An error of 5^o can be considered for the values. The above measurements were taken for pillar structures 40 um high.

In order to increase the possibility of the magnetic actuation were used pillars with higher aspect-ratio. Patterns with interpillar distance of 77 um were produced since as it is obvious from Figure 4 they exhibit higher WCA changes with respect to the others. The resulting SU-8 pillars of height of 195 μm had an initial WCA and hysteresis values of 113° and 24° respectively, which after the iron-oxide and the PTFE spray-coating layer showed a significant decrease in the hysteresis value and a significant increase in the WCA, rendering the specific sample self-cleaning. The results are presented in table 2.

Material	**WCA/^{o}**	**Hysteresis/^{o}**
SU-8	113	24
SU-8/Fe_2O_3	150	30
SU-8/ Fe_2O_3/PTFE	170	4

Table 2: WCA and hysteresis values, before and after the coatings.

On this sample it was subsequently performed the experiment for the directional water drop movement under magnetic field as shown at figure 5. A drop was placed onto the pillars which were positioned at a small tilting angle. As the magnet was moved under the pillars and towards the drop, the former were actuated due to magnetic attraction, causing the movement of the drop. This movement is demonstrated by the frames presented in figure 5.

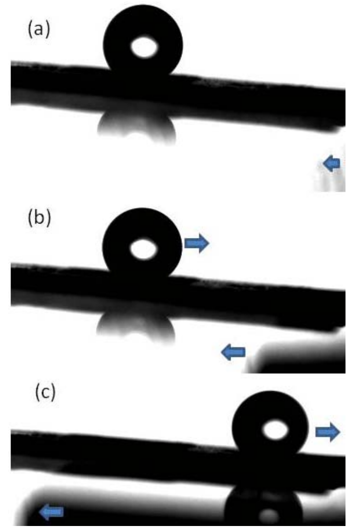


Figure 5: Demonstration of the water drop movement. In the lower part of the images it is shown the magnet (0.5 T) moving from right to left underneath the sample.

4 CONCLUSIONS

We have fabricated super-hydrophobic and self cleaning magnetic surfaces with well organized roughness both in micro- and nano-scale. A water drop placed on this type of surfaces can be successfully moved upon an external magnetic field. These results are very encouraging for the development of magnetically actuated microfluidic devices.

REFERENCES

[1] Shirtcliffe N., Aqil S., Evans C., McHale G., Newton M.I., Perry C.C., Roach P., J. Michromech. Microeng., 14, 1384-1389, 2004
[2] Caputo C., Cortese B, Nobile C., Salerno M., Cingolani R., Gigli G., Cozzoli P.D., Athanassiou A., Adv. Funct. Mater., 19, 1149-1157, 2009
[3] Liu J., Cai B., Zhu J., Ding G., Zhao X., Yang C., Chen D., Microsystem Technologies, 10, 265-268, 2004
[4] Hong L., Pan T., Journal of Microelectromechanical Systems, 19, 246-253, 2010
[5] http://www.microchem.com/products/su_eight.htm
[6] Fragouli D., Buonsanti R., Bertoni G., Sangregorio C., Innocenti C., Gatteschi D., Cozzoli P.D., Athanassiou A., Cingolani R., ACS NANO, 4, 1873-1878, 2010