



Modification of paper using polyhydroxybutyrate to obtain biomimetic superhydrophobic substrates

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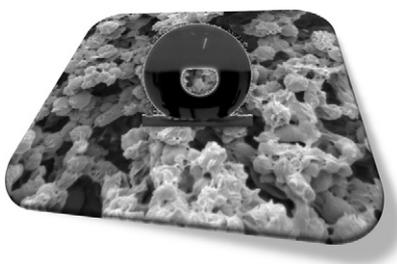
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HIGHLIGHTS

- ▶ Superhydrophobic paper-based substrates were obtained by a simple surface modification.
- ▶ The final material kept the main handling/mechanical properties of the original paper.
- ▶ The wettability of the substrates can be controlled through argon plasma treatment.
- ▶ It is possible to pattern wettable regions in the superhydrophobic-based paper.

GRAPHICAL ABSTRACT



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ABSTRACT

Inspired in nature, the creation of synthetic superhydrophobic surfaces is nowadays a major object of study, with many potential applications in different fields. The fabrication of such substrates has been dominated by the use of non biodegradable and poorly flexible materials, using expensive and complex procedures. To overcome this issue, we propose a simple concept for fabricating low-cost, biodegradable, and flexible biomimetic superhydrophobic materials, using paper as substrate. The methodology includes the precipitation of poly(hydroxybutyrate) (PHB) on the surface of cellulose fibers of papers using a phase separation process. The obtained surfaces showed a rough texture, at both micro and nano length scales and an apparent water contact angle of $153.0 \pm 0.7^\circ$. Furthermore we showed that argon plasma treatment increases the surface wettability and it is possible to control the wettability in certain regions by using adequate hollowed masks. Such findings could be used for the production of cheap open-microfluidic or lab-on-chip devices, using materials from renewable resources.

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1. Introduction

The development of new devices for microfluidics, electronics, biosensors, environmental and biomedical applications requires often substrates exhibiting low adhesion and non-wetting properties [1–4]. Many surfaces found in nature exhibit highly hydrophobic and self-cleaning properties, including the leaves of plants such as lotus, the wings of cicada and butterflies or the water strider's leg, which have inspired many researchers in

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understanding the underlying phenomena and develop synthetic surfaces with similar properties [5–8].

It has been recognized that superhydrophobic surfaces (apparent water contact angle, WCA, higher than 150°) must combine two essential properties: (i) surface roughness, especially hierarchically roughness at the nano and micro scale-levels and (ii) low surface energy [1]. Synthetic superhydrophobic substrates have been produced by a variety of methodologies, from chemical modifications treatments that lower the surface energy (normally adding fluorides compounds to the surface) [9] to the introduction of a double-scale of roughness features, mimicking the lotus leaves topography [4,7,10–12]. Superhydrophobic surfaces have been produced using metallic, inorganic and polymeric substances. Many applications do not require long-term use of such kind of substrate, such as package materials, platforms for diagnosis and biosensing or a series of biodegradable devices for biomedical and environmental applications [13–15]. Biodegradable or disposable superhydrophobic substrates produced by natural or synthetic polymers have not been extensively developed. For example, substrates from poly(L-lactic acid) [16,17] or chitosan derivatives [18] fabricated using a phase separation method, were reported in the literature. The important role of paper in the scientific and technological world has been recognized mainly to its effective potential as a cheap, biodegradable, versatile and flexible substrate, to be used, for example, in microfluidic analytical devices or in a series of other lab-on-paper applications [13,19,20]. Concretely, through the pioneered work of Whitesides and co-workers, 2D or 3D structures based on a hydrophobic–hydrophilic patterned paper were suggested for low cost bioassays devices [21,22]. We hypothesize that such lab-on-a-chip devices, as well as substrates for packing, sensors or paper-based MEMS, could be highly improved if one could start with surfaces exhibiting extreme wettability. A few attempts reported the preparation of paper showing superhydrophobic characteristics: Yang and Deng coated paper with silica nanoparticles that were then chemically modified with 1H, 1H, 2H, 2H-perfluorooctyltriethoxysilane [23]; Balu et al. modified the paper surface through selective etching via oxygen plasma followed by the deposition of a thin film from pentafluoroethane [24]. Such methods permitted to obtain substrates exhibiting WCAs higher than 150° . In this work we present a simpler method of modifying paper by depositing a thin film of a biodegradable polymer, poly(hydroxybutyrate) (PHB), with an adequate micro/nanostructure to provide superhydrophobic characteristics to the obtained substrate. The generation of such particular topography in PHB is achieved through a phase separation methodology, which was applied before in poly(L-lactic acid) [17] and polystyrene [25].

Our inexpensive and simple bench-top method can be easily accessible to virtually any researcher and may be scaled-up to higher massive productions. Moreover we show that further plasma treatment on such substrates permits to decrease the WCA down to superhydrophilic regime in a controlled way, just by adjusting the exposure time. The plasma modification may be spatially controlled in order to confine such modification in certain regions of the substrate, enabling patterning hydrophilic lines surrounded by superhydrophobic regions that could be used to generate gradients in fluid stripes [26] or in devices for open-microfluidic applications [2,25,27].

2. Materials and methods

2.1. Materials

Commercial 80 g/m² copy paper, purchased in Staples® Office Center, was used as supporting substrate. Commercial grade

poly(hydroxybutyrate), PHB, with a melting point of 173°C , was kindly supplied by Biomer in the form of a very thin powder. Chloroform and ethanol, with 99% and 99.5% of purity, were supplied by Carlo Erba Reagent and Pancreac, respectively.

2.2. Production of superhydrophobic paper

Squares of 4 cm² were cut from A4 sheets of commercial copy paper and were immersed in chloroform for at least 6 h, to extract any possible additives soluble in the solvent. Then the samples were immersed for 6 h in a 7.5% (w/v) solution of PHB in chloroform, followed by an immersion in a coagulation bath, formed by a mixture of 85/15 (v/v) of ethanol and water, during 12 h. Finally the samples were placed in a glass surface and dried at room temperature.

2.3. Surface modification

A Plasma Prep5 chamber (Gala Instruments, Germany) was used to modify the surfaces wettability. The pressure was kept between 0.16 and 0.2 mbar. All the samples were exposed in an argon working atmosphere with an applied voltage of 2.2 V. The exposure time varied between 5 and 180 s. After the treatment the samples were stored in a dry environment until characterization.

Wettable channels were patterned in the initial superhydrophobic paper – see scheme in Fig. 1. The samples were covered with two glass slides, spaced 1 mm between them, and treated with argon plasma irradiation. The exposed region of the substrate not covered by the glass is expected to acquire more wettable characteristics.

2.4. Surface characterization

The morphology and the topography of samples surface were analyzed by scanning electron microscopy (SEM), using a JEOL JSM 820 microscope. The surfaces were sputter coated before with a thin gold layer.

The wettability of the prepared surfaces was evaluated by WCA measurements [28], using an OCA15+ goniometer from DataPhysics (Germany), at room temperature, with a conventional sessile drop method. A 5 μl droplet of HPLC grade water was deposited on the surface. The shape of each droplet was recorded and analyzed using the SCA 20 software. At least three measurements were taken for each sample.

X-ray photoelectron spectroscopy (XPS) analysis was performed using a VG-Microtech Multilab 3000 spectrometer (VG Scientific) equipped with a hemispherical electron analyzer and an X-ray tube with Mg and Al anodes.

3. Results and discussion

With the immersion of the paper samples inside the chloroform solution containing PHB, the specimens started to soak, permitting PHB to penetrate into the paper fibers network. The immersion of these samples in the coagulation bath induced the precipitation of the hydrophobic polymer, observed mainly in the surface as a sphere-like aggregate structure (see Fig. 2A and B). Moreover, it is possible to visualize some amount of PHB embedded between the cellulose fibers (see labels in Fig. 2C and D), revealing that this hydrophobic agent stays attached to the entire substrate. The obtained structure, achieved after the modification with PHB, clearly contrasts with the fibrous texture of the original paper (see Fig. 2E).

The protocol to induce PHB precipitation involved the mixture of a solvent and a non-solvent of PHB: chloroform and a mixture of ethanol and water, respectively. When we immersed the polymer solution into a coagulation bath a separation in two phases occurred: a PHB-rich phase and a PHB-poor phase [25,29,30]. As

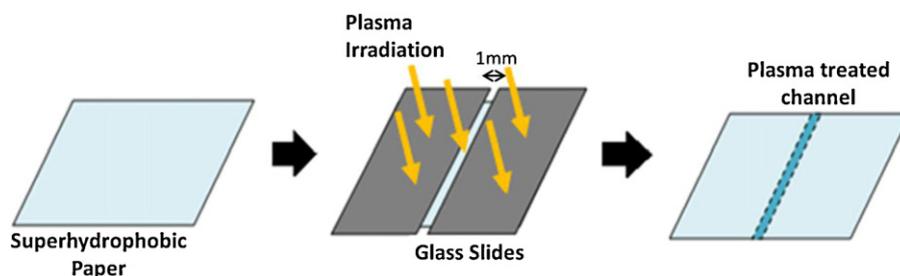


Fig. 1. Schematic representation of the patterning process of superhydrophobic paper. The glass slides limited the treatment area to channel-like regions.

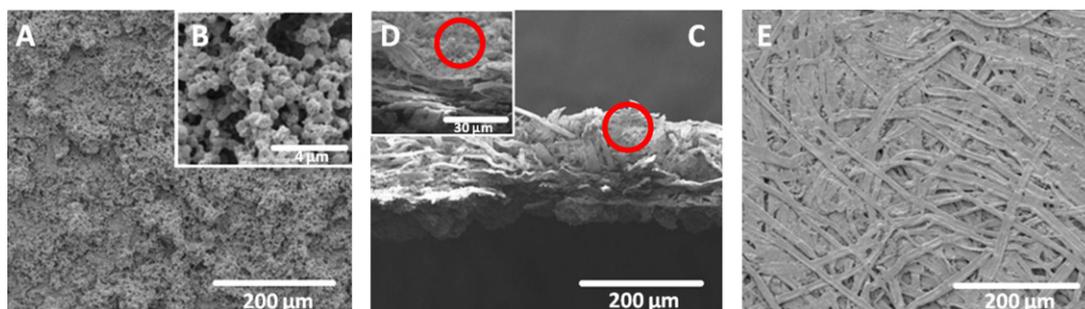


Fig. 2. SEM images of (A) the surface of superhydrophobic paper and the corresponding magnification (B). (C) The transversal fracture, obtained in liquid nitrogen, of the superhydrophobic paper and corresponding magnification (D). (E) Representative SEM image of the commercial copy paper used to prepare the substrates.

chloroform and ethanol are miscible [31], the solvent in the polymer solution is exchanged by the non-solvent (ethanol) and the PHB precipitation can occur [32]. Consequently, in the PHB-poor phase, polymer nuclei are generated by precipitation. Meanwhile, the PHB-rich phase aggregated around these nuclei, in order to decrease the surface energy [25,33]. During polymer precipitation in the rich PHB phase, a continuous deposition of sphere like structures takes place (Fig. 2B). Due to the low miscibility between the chloroform and the water (less than 0.8 g/100 ml) [34], the presence of water in the coagulation bath acts like a selective barrier, avoiding the PHB spreading off the paper. However, the ethanol is highly miscible with both water and chloroform [31,34] so the demixing liquid–liquid happens fast enough, inducing the precipitation of PHB.

The original paper presented a WCA of $110.4 \pm 0.8^\circ$ (Fig. 3A). Upon modification with PHB, the WCA rises up to $153.0 \pm 0.7^\circ$ (Fig. 3B), being clearly in the superhydrophobic regime. To evaluate the robustness of the prepared superhydrophobic substrates we carried out a simple non-standard mechanical test with the finger [24], forcing it down the surface. Even supposing that the paper presents itself some brittleness, and for that inspires a careful manipulation, this trial reproduces the indispensable handling of the substrate: the WCA changes from $153.0 \pm 0.7^\circ$ to $150.2 \pm 3.8^\circ$, indicating that the prepared substrates exhibit a good robustness behavior. The little discrepancy between the WCAs and the increasing of the standard deviations could be consequence of some

accumulation of dust or oil in the surface, derived from the finger contact.

With further argon plasma treatment one can decrease the WCA of the superhydrophobic surfaces; using exposure times of the order of seconds one can reach hydrophobic surfaces (Fig. 3C) but for higher exposure times it is possible to obtain superhydrophilic surfaces (Fig. 3D). Upon modification with plasma we measured the WCA of the samples after different time points (1 day, 3 days and 5 days) and during this period no significant recovery of hydrophobicity was observed.

The obtained superhydrophobic surfaces were treated with argon plasma from 5 to 180 s. Even for the lowest treatment time (5 s of plasma treatment), the WCA decreased down to the hydrophobic regime ($141.0 \pm 1.7^\circ$) – see Fig. 3C. With increasing treatment time the sample became clearly more wettable. As the substrate is based on cellulose, a material that permits some water swelling [24,35], we investigated the stability of the deposited water droplets on the modified substrates: Fig. 4A shows the time evolution of the WCA of the droplets of water deposited in surfaces previously subjected to plasma treatment for different times. For the unmodified superhydrophobic substrate and for exposure times of 5 s no changes in the WCA are detected with the contact time of the droplet with the surface. However surfaces with longer exposure time to plasma have enough wettability properties that permit the diffusion of water molecules inside the cellulose structure: after a certain time period, which decreases with

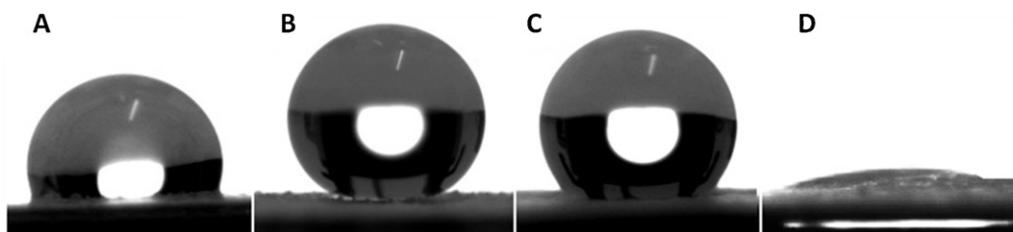


Fig. 3. Representative images of a 5 µl water droplet sitting over: (A) commercial copy paper; (B) superhydrophobic copy paper; superhydrophobic paper treated with (C) 5 s (D) and 180 s of argon plasma irradiation.

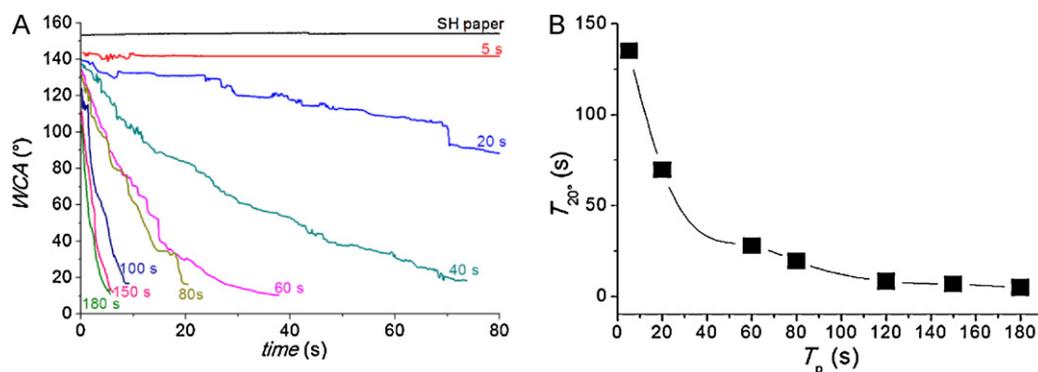


Fig. 4. Graphical representation of: (A) evolution in time of the measured WCA of a 5 μ l water droplet dispensed on surfaces of initial superhydrophobic paper treated with plasma for different times (in seconds); (B) the time needed for the different water droplets to reach a WCA of 20° as a function of the plasma treatment time, T_p .

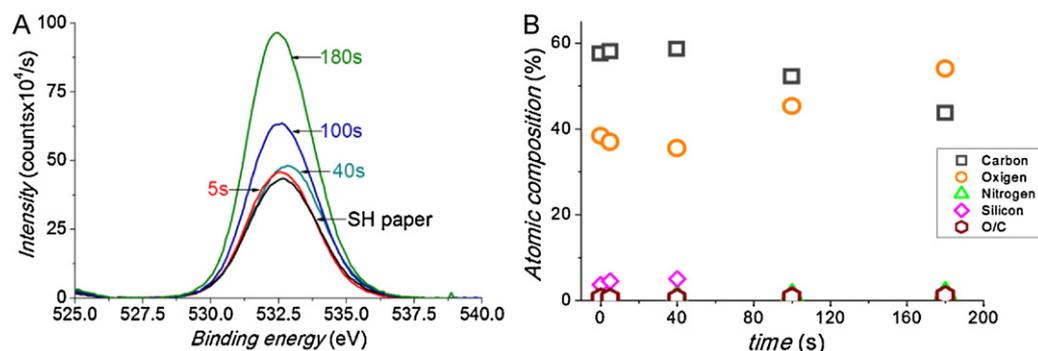


Fig. 5. (A) O1s photopeaks for the samples under study and (B) surface atomic composition of samples treated with plasma for different exposure times.

increasing plasma treatment time, the region of the surface close to the water droplet gets more wettable and the measure WCA starts to decrease. Such phenomena could be explained by the disruption of the hydrogen bonds [36] within amorphous fraction of the cellulose fibers upon water absorption that renders the substrate more hydrophilic. The 5 s treatment is not sufficient to trigger this process. We can define an arbitrary threshold value of WCA below which the surface is clearly hydrophilic; Fig. 4B shows the time necessary for a droplet deposited onto the surfaces treated with different plasma irradiation times to reach a WCA of 20°. For treatment times above 60 s the spreading of the water droplet is quite fast, being shorter than 20 s. Note that the same trend would be observed if other thresholds value either than 20° would have been chosen.

The surface chemistry of the treated samples was analyzed by using XPS. Fig. 5A shows representative O1s photopeaks. It is clear that there is an evident evolution of the XPS photopeaks for binding energies in the range of 525–540 eV, showing an increase of the oxygen content as a function of time. The surface composition of the samples was obtained from the XPS data. Fig. 5B shows the results as a function of the treatment time. The non-treated sample is mainly composed by carbon and oxygen, but small amounts of silicon, as a contaminant, and nitrogen are also detected. For times of treatment around 100 s it is observed a significant and relative decrease in carbon and a noticeably increase in oxygen on the surfaces. In fact the O/C ratio increases from about 0.7 to around 1.3 for the sample treated for 180 s. The amounts of silicon and nitrogen keep very small for all the analyzed samples. Therefore, the

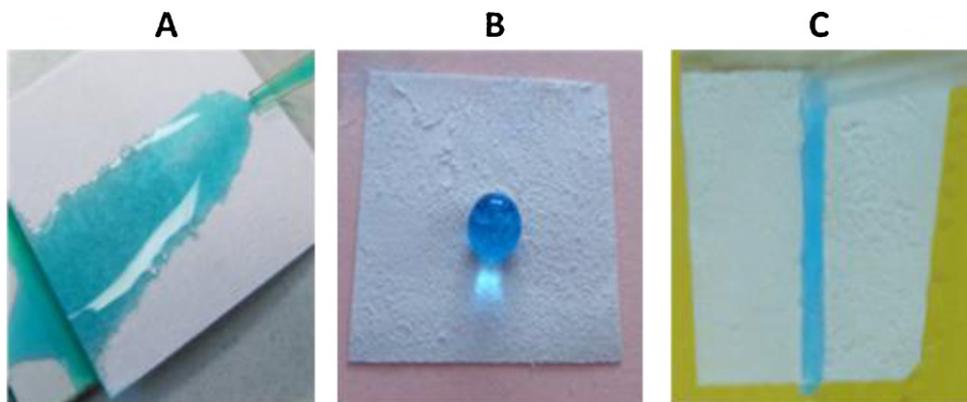


Fig. 6. Representative images of a 0.815 ml/min flow of blue colored water onto a (A) commercial copy paper; (B) superhydrophobic paper based substrate and (C) open hydrophilic channel of 1 mm of width patterned in a superhydrophobic paper substrate. All substrates were slightly lean so that the water could flow by the effect of gravity. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

plasma treatment increased the amount of oxygen on the surface, increasing the quantity of C–O, C=O and COOR moieties [37]. This increment caused a significant reduction of both WCA value and the times to reach low WCAs [38] as it was observed in Fig. 4. It should be noticed that the plasma treatment did not lead to appreciable changes in the topography of the samples, as seen by SEM (data not shown).

By controlling in space the exposure of argon plasma, it should be possible to pattern the superhydrophobic paper with more wettable regions. For the proof-of-concept we used two slide glasses to create an open channel shaped mask (Fig. 1). By controlling the treatment time it was possible to create more wettable paths with the exposed geometry onto the superhydrophobic surface due to the oxidation of the uncovered area. Such patterned superhydrophobic substrates were proposed before as open-microfluidic devices, in which water could flow along the patterned channels without transposing the confined geometries, due to the high contrast in surface tension [25]. We chose 5 s plasma treatment to pattern the substrate because it is sufficient to create a contrast of wettability without changes in WCA with time (as it is observed in Fig. 4A). We compared the behavior of the flow of water in different substrates: commercial copy paper, superhydrophobic paper and the open-channel patterned substrate treated with 5 s of plasma treatment – see Fig. 6.

In the smooth paper surface – see Fig. 6A – we can observe the increasing of the drop size as it advances over the leaning surface, spreading in both lateral directions, with no spatial control, due to the progressive absorption of water by the paper.

In the superhydrophobic surface the release of water droplets is hampered by the repellence of the substrate. As expected, the droplet roll off the surface – see Fig. 6B.

For the channel-patterned substrate the drop had preference for the treated path, due to the fact that the patterned region is more wettable. Therefore, it was possible to retain and control the water flow along the confined geometry – see Fig. 6C.

4. Conclusions

This work proposed a new solution to fabricate superhydrophobic paper-based substrates, involving a simple phase separation approach, using a natural origin polymer (PHB). The results confirmed that the methodology is able to prepare robust, flexible, non hazardous and non wettable paper-based surfaces, which can be applied in different biomedical and environmental applications. The wettability of the obtained substrates can be controlled by adequate argon plasma treatment. Such surface modification capability provides a powerful tool to achieve easy, inexpensive and reliable substrates, which could be patterned with more wettable regions, just by exposing surface selected areas to an argon plasma treatment. The created paths permit the control of the water flow just using the effect of gravity.

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