Spontaneous Liquid Flow in Microfluidic Systems by UV Irradiation of the Hybrid Polymer/TiO_2 Nanorods Channels

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ABSTRACT

A method for enhancing the surface wettability of PDMS microchannels used in microfluidic devices, is presented. Colloidal TiO_2 nanorods are mixed in a PDMS solution that was used subsequently to realize parallel microchannels, through a replica molding procedure. TiO_2 has the intrinsic capability of increasing dramatically its hydrophilicity upon UV irradiation. Due to this property, incorporating TiO_2 nanofillers into the PDMS microchannels we manage to induce their hydrophobic-to-hydrophilic conversion upon UV irradiation. This conversion is essential for water to fill the microfluidic channels, in contrast to what happens for the non-irradiated nanocomposite or pure PDMS channels, which are characterized by high hydrophobicity and do not allow water to penetrate. The reversibility of the wettability changes permits to the microchannels to recover their original hydrophobicity.

Keywords: nanocomposites, TiO_2 nanorods, microfluidics, reversible wettability

1 INTRODUCTION

Microfluidic systems are increasingly used for transporting, storing, mixing, reacting, and analyzing small amounts of diverse liquids. A major challenge in their operation is the controlled motion of liquids, achievable through capillary forces in the case of microstructures [1], that are limited by the increased interfacial forces as the structures are miniaturized. Among different materials, poly(dimethylsiloxane) (PDMS) has become the most popular choice [2] because of its elasticity, flexibility, non-toxicity, physical and chemical stability over a wide range of temperatures (-50°C to 200°C), oxygen permeability etc. Nevertheless, its high hydrophobicity (WCA$\geq$110°) makes the introduction of aqueous solutions by spontaneous capillary forces into PDMS-based microchannels very difficult. For this reason, different techniques have been adopted in order to increase the PDMS hydrophilicity [3-5].

The use of smart materials that can respond to external stimuli by reversibly changing their surface properties has been employed several times, [6, 7] for the taylored enhancement of the hydrophilicity of surfaces. Light is one of the most important external stimuli used [8], permitting easy miniaturization of the microfluidics devices, since the use of valves, pumps, and similar components, difficult to miniaturize, can be avoided. For this purpose several semiconductive oxides such as TiO_2, SnO_2, ZnO and V_2O_5 can be used, which change their contact angle upon UV irradiation, and recover their initial wettability characteristics after dark or vacuum storage.

Previously, we have shown that nanocomposite surfaces of PMMA mixed with titanium dioxide (TiO_2) nanorods (NRs) show spontaneous water drop movement upon gradual UV irradiation of adjacent surface areas with increasing time [9]. Getting one step forward, in this study we present a technique to modify the wettability of PDMS microfluidic channels in order to achieve their spontaneous water filling. We use again colloidal TiO_2 NRs as nanofillers in PDMS microchannels supported by glass substrates. A water droplet, released at the entrance of the microchannels, cannot enter into the device when the channels consist of PDMS or of non-irradiated TiO_2 NRs/PDMS nanocomposite. The produced nanocomposite channels exhibit, upon UV light irradiation, increased hydrophilicity. For this reason the water drop spontaneously fills the channels after UV irradiation. This procedure is reversible, since upon storage in vacuum the initial hydrophobicity of the irradiated microchannels is fully recovered.

2 MATERIALS AND METHODS

All chemicals were used as received. PDMS (Sylgard 184) was purchased by Dow Corning, Midland, MI. The TiO_2 NRs solution in toluene was prepared as described elsewhere [10], in order to obtain oleic acid-capped NRs with a mean length of 20 nm and an average diameter of 3 nm. 24 mm x 24 mm glass microscope slides were used to create the fourth wall in the microfluidics system. All solvents used were purchased from Sigma-Aldrich.

Solutions of PDMS (A:B 1:10) and TiO_2 NRs 95 wt.% and 5 wt.%, respectively, were prepared in toluene. The solutions were stirred and left under dark for several minutes to equilibrate and then used to realize the microfluidic systems according to a standard replica molding procedure. In particular, the devices were formed by four channels of height 3 μm and length 20 μm each and were obtained by in situ polymerization (75°C for 20 min) of the abovementioned solutions, using templates realized by photolithography.

The hydrophilicity enhancement of the nanocomposite systems was achieved by irradiating the internal part of the prepared microchannels for 4 h with a pulsed Nd:YAG laser at 355 nm (energy density of 7 mJ cm^{-2}, repetition rate of 10 Hz, pulse duration of 4-6 ns). We achieved the complete recovery of the initial wettability of the samples by placing them in vacuum at a pressure of $3x10^{-3}$ mbar for 48 h.

For the wettability characterization of samples water contact angle (WCA) measurements were carried out with a KSV CAM200 goniometer. Distilled water was dispensed using a microsyringe. The typical drop volume was around 1 μL. For each sample the contact angle value was obtained as an average of 6 measurements recorded on different adjacent areas of the surface.

Fourier Transform Infrared (FT-IR) spectroscopy measurements in the 3700-3000 cm-1 spectral range were carried out using a VERTEX 70 apparatus in transmittance mode at a resolution of 4 cm^{-1}.

The study of the liquid motion have been conducted by releasing a 5 μL water drop at the edge of the microchannels, which were then spontaneously filled by capillary action.

3 RESULTS AND DISCUSSION

3.1 Characterization of the wetting behavior of the PDMS/TiO_2 nanocomposites

Before the realization of the microfluidic channels of PDMS-TiO_2 NRs an analytical characterization of the wetting properties of this systems was performed. In particular, we performed WCA measurements on flat PDMS-TiO_2 NRs nanocomposite samples and pure PDMS samples before and after their irradiation with UV laser pulses. The results can be seen in Figure 1 where are illustrated the WCA values measured on PDMS samples with and without NRs, after their preparation (1), after subsequent UV laser irradiation for 4 h (2), and after 48 h under vacuum conditions (3). The WCA of the pure PDMS remains stable at 116°±2° after the UV irradiation and the vacuum treatment process, demonstrating that the TiO_2 nanofillers are exclusively responsible for any wettability differences induced by light. In the case of PDMS/TiO_2 NRs nanocomposites, the initial WCA is 105°±2°, slightly lower than the one measured on pure polymer samples. The decreased WCA values of the nanocomposite samples can be attributed to the increased surface hydrophilicity due to the TiO_2 NRs present on the sample's surface (as demonstrated by independent WCA measurements on films of TiO_2 NRs deposited by drop casting on glass and silicon substrates, that gave an average WCA value of 72°±2°), in combination with the increased nanoroughness that the NRs can induce to the samples [11].

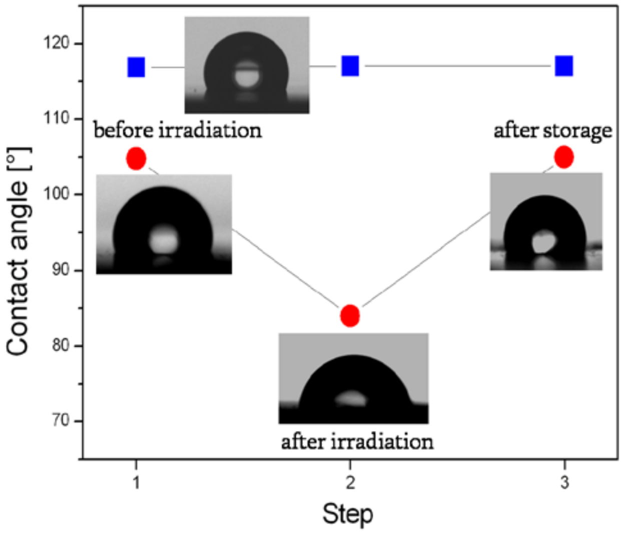

Figure 1. WCA measurements performed on PDMS/TiO_2 NR-samples during a cycle of UV irradiation and vacuum storage (●) and on PDMS samples without NRs during the same UV-irradiation/storage cycle (■). The thickness of each point represents the experimental error of the measurements. Pictures of the water drops lying on the nanocomposite surface are shown at every step of the process.

The UV irradiation of the PDMS/TiO_2 NRs nanocomposites (step 2 in Figure 1) causes a decrease in the WCA by 20°, leading to a contact angle of 84°±2°, due to the UV-induced hydrophilicization of TiO_2 attributed to a mechanism that will be discussed in more detail later on. Finally, after a short vacuum storage period (step 3 in Figure 1), the samples recover their initial hydrophobic character. The reversible wetting cycles were repeated many times on various nanocomposite films, without any apparent fatigue (Figure 2).

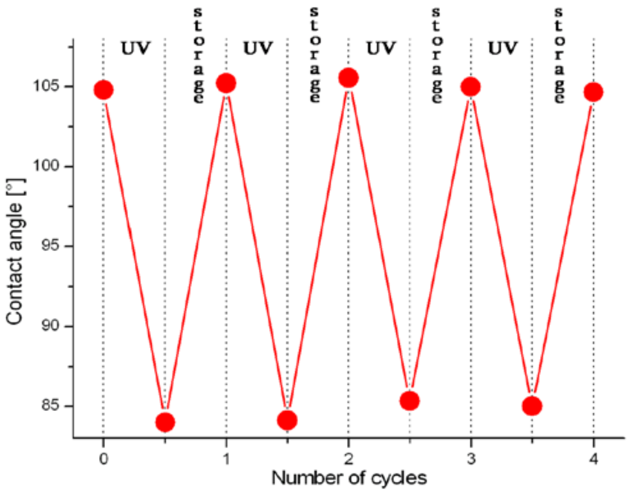

Figure 2. Reversible wettability changes during cyclic alternations of UV illumination and vacuum storage.

The UV-dependent reversible hydrophilicization mechanism is elucidated through FT-IR measurements. The relevant data are presented in Figure 3. The results reveal remarkable changes only in the OH band (3100-3650 cm^{-1}) of the nanocomposites, whereas the rest of the bands remain unaffected. FT-IR measurements on pure PDMS polymer showed no changes before and after UV irradiation.

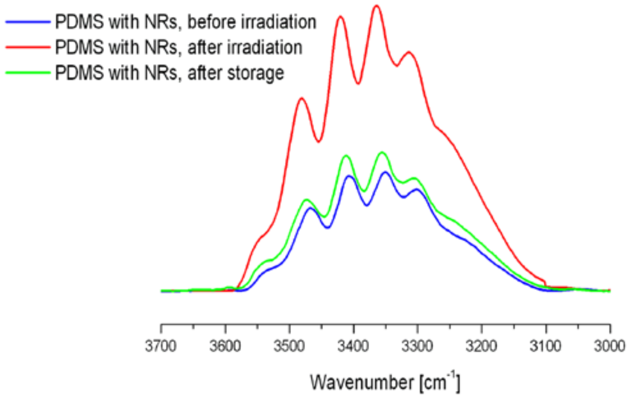

Figure 3. FT-IR spectra of PDMS/TiO_2 NRs films throughout a cycle of UV irradiation and vacuum storage process in the 3700-3000 cm^{-1} range.

Figure 3 reveals that upon UV irradiation a considerable increase occurs in the ν(O–H) vibrations most likely due to the convoluted contributions from growing TiO–H species and physisorbed H_2O at ~3400 cm^{-1} and ~3200 cm^{-1}, respectively, suggesting an increase in hydroxylation on the exposed TiO_2 NRs facets. The OH species introduced to the surface upon photoirradiation are metastable, and thus, upon vacuum storage the initial surface hydroxylation degree is recovered. The mechanism previously described in other works [9, 11] is in full agreement with our findings. Briefly, the holes generated on the TiO_2 surface upon UV excitation, lead to the formation of oxygen vacancies, to which ambient water molecules coordinate, forming a hydrophilic surface, as actually demonstrated by the decrease in the WCA measured in our experiments. The initial hydrophobic state is restored during the vacuum storage, since atmospheric oxygen replaces the OH groups previously implanted onto the surfaces [10-13].

3.2 Spontaneous capillary motion of water in PDMS/TiO_2 NRs microchannels

The possibility to create hydrophilic PDMS-based nanocomposite surfaces, characterized by reversible changes in their surface wettability, by exploiting the UV-dependent switchable wetting properties of TiO_2 NRs, permitted us to realize microfluidic devices in which spontaneous liquid motion can occur. Our microfluidic devices consist of four parallel microchannels, formed by three PDMS/TiO_2 NRs walls sealed with a glass substrate (Figure 4a). The water filling experiment presented in Figures 3b and 3c demonstrates that a water droplet released at the entrance of the microchannels, spontaneously fills the channels or not, depending on the their hydrophilicity/hydrophobicity characteristics.

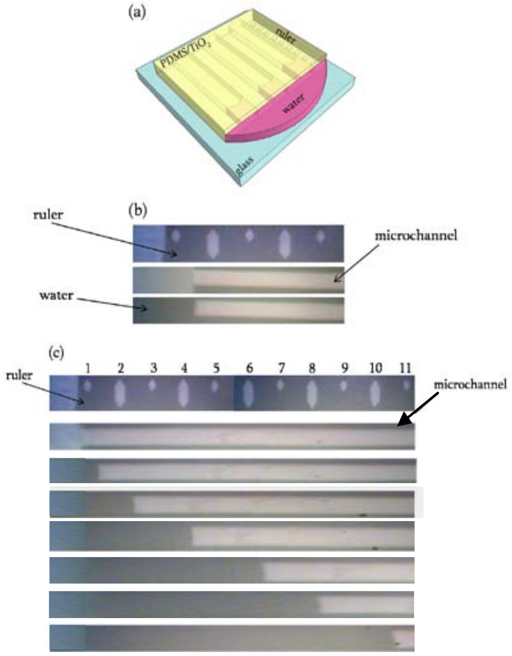

Figure 4. (a) Schematic representation of the microfluidic device and the filling experiment: a drop is released at the edge of the microchannels is order to fill the system by the capillary action. (b) Photographs of the filling process from a non-irradiated nanocomposite microchannel: when the

water is put in contact with the system, it does not fill the microchannel because of the high hydrophobicity. (c) Photographs of the filling process on an irradiated nanocomposite microchannel: thanks to the increased PDMS wettability, the water eventually fills completely the microchannel.

The following equation describes the relation between the flow rate of a liquid in a channel, the geometry of the capillary and the properties of the fluid used [14]:

$$\frac{dz}{dt} = \frac{R\gamma_{LV}\cos\theta}{4\eta z} \tag{1}$$

where R is the radius of the capillary, η is the viscosity of the fluid, z is the length covered by the liquid in time t, γ_{LV} is the interface tension between the liquid and the vapor, θ is the contact angle between the liquid and the solid. It can be seen that the rate of filling is inversely proportional to the length of capillary that is being filled. Thus, the filling rate decreases as the liquid fills the capillary.

According to equation (1) the PDMS-based microchannels should exhibit a contact angle <90° in order to be spontaneously filled by water. Therefore it is necessary to render the hydrophobic PDMS hydrophilic. Taking advantage of the results presented in section 3.1 we prepared microchannels of PDMS/TiO_2 NRs nanocomposites and we irradiated their internal surfaces with UV light, in order to enhance their surface hydrophilicity.

In fact, as shown in Figure 4 when the water is in contact with pure PDMS microchannels or with a non-irradiated nanocomposite device, it does not fill the channels, because of the high hydrophobicity (WCA=116°±2° and 114°±2°, respectively) (Figure 4b). On the contrary, the UV irradiated nanocomposite microchannels that are characterized by a lower contact angle (WCA=84°±2°) show continuous and spontaneous water motion (Figure 4c).

4 CONCLUSIONS

In this work, a novel approach for increasing the PDMS surface hydrophilicity is proposed, incorporating TiO_2 NRs in it and exploiting the UV-dependent switchable wettability properties of TiO_2. We realized microfluidic devices of PDMS and PDMS-TiO_2 NRs nanocomposite that do not allow water to penetrate into their microchannels due to their hydrophobic character. Upon UV irradiation the microchannels are spontaneously filled by the water, driven by the capillary forces, due to their obtained hydrophilic character. The reversibility of the wettability changes eventually permits to the samples to recover their original hydrophobicity and be reused

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