

# Layer by layer control of wettability in nanocomposite films

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## ABSTRACT

Photopolymerized nanocomposite films of polystyrene and TiO<sub>2</sub> nanorods are found to change their surface wettability characteristics in a controlled manner, depending on both the substrate used and on the number of film layers realized. The constituents of the nanocomposite solutions, namely styrene monomers and TiO<sub>2</sub> nanorods, interact differently with the surface on which they are deposited, depending on its wettability. This interaction influences their dispersion along the depth and on the surface of the photopolymerized film, impacting on its wetting properties. We demonstrate that the diverse amount of TiO<sub>2</sub> nanorods exposed each time on the surface of the final film, which depends on the wettability of the surface lying underneath, is responsible for the layer-by-layer alternated surface characteristics. Moreover, due to the presence of TiO<sub>2</sub> nanorods on the sample's surface, the wettability characteristics can be tuned in a reversible manner upon UV irradiation and vacuum storage cycles.

**Keywords:** photopolymerization, nanocomposites, surface wettability, TiO<sub>2</sub> nanorods

## 1 INTRODUCTION

In recent years the need for materials with tailored properties for specific applications has led to the synthesis of polymeric nanocomposites, which exhibit a combination and an enhancement of the properties of the individual components. In particular, these materials are very useful in applications which need to modify and control the surface wettability [1, 2]. Versatile approaches, including appropriate external stimuli, are frequently used for the realization of smart materials with controlled and switchable surface wettability. Light is one of the most promising external stimuli [3], and for this purpose several semiconductive oxides such as TiO<sub>2</sub>, SnO<sub>2</sub>, ZnO and V<sub>2</sub>O<sub>5</sub> are used, which increase their hydrophilicity upon UV

irradiation and recover their initial wettability characteristics after dark or vacuum storage [4, 5].

Here we propose an alternative method to modify and control the surface wettability properties of a specific material, by creating nanocomposite films on substrates with different surface properties, where the number of the deposited layers defines the final hydrophilicity of the coating. In particular, we prepared samples with one, two, or more successive layers of photopolymerized nanocomposite films containing titanium dioxide (TiO<sub>2</sub>) nanorods (NRs) as nanofillers and polystyrene as polymeric matrix, while the substrates used were glass and silicon. The chosen substrates exhibit different chemical affinity with the NRs affecting their distribution in the matrix, and thus, the surface properties of the resulting material. Indeed, the hydrophilicity of the nanocomposites increases with the number of NRs exposed on the samples' surface.

## 2 EXPERIMENTAL METHODS

### 2.1 Samples Preparation

TiO<sub>2</sub> colloidal NRs of 20 nm length and 3 nm diameter were synthesized as described elsewhere [6]. Toluene solutions containing 5% wt NRs, 94% wt styrene (ST) and 1% wt photoinitiator (PI) (IRGACURE®1700) were prepared to be subjected to photopolymerization. The first layer of the samples was prepared by spin coating 200  $\mu$ L of the abovementioned solutions on glass or silicon substrates at 1000 rpm for 20 s. Then, in order to obtain the nanocomposite coating, the samples were irradiated with the third harmonic of a pulsed Nd:YAG laser (Quanta-Ray GCR-190, Spectra Physics), with an energy density of 10.5 mJ·cm<sup>-2</sup> ( $\lambda$  = 355 nm, pulse duration = 4-6 ns, repetition rate = 10 Hz), for different times depending on the substrate. For the subsequent layers 40  $\mu$ L of the same solution were added by drop casting onto the previously photopolymerized layer. After the photopolymerization, the samples were washed with methanol and dried in ambient

dark condition. Afterwards, to enhance the hydrophilicity of the samples due to the TiO<sub>2</sub> NRs exposed on their surface, we irradiated the prepared films for 90 min with a pulsed Nd:YAG laser at 355 nm, (energy density of 7 mJ·cm<sup>-2</sup>, repetition rate of 10 Hz, pulse duration of 4-6 ns). We achieved the complete recovery of the initial wettability of the films by placing them in vacuum under ambient dark conditions at a pressure of 3x10<sup>-3</sup> mbar for 150 h.

## 2.2 Samples Characterization

Adhesion force measurements were carried out in water with a JPK NanoWizard II AFM system. A cantilever with a triangular soft tip made of silicon nitride, with a nominal elastic constant of 0.06 N m<sup>-1</sup>, was used, functionalized with thiol-terminated molecules. For each sample the adhesion force values were obtained analyzing 400 points on 4 different areas.

Measurements of the apparent water contact angle (WCA) were carried out with a KSV CAM200 instrument. Distilled water was used as the liquid for these tests and 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.

## 3 RESULTS AND DISCUSSION

### 3.1 Single-Layer Nanocomposite Films

Using the photopolymerization technique, we produced nanocomposite films of PS incorporating TiO<sub>2</sub> NRs with final thickness of 430±50 nm on glass and silicon substrates. Interestingly, all the nanocomposite films formed onto the two substrates show diverse surface properties, depending on the different distribution of the samples components onto the surface of the films, related to their interaction with the underlying layer.

To verify this hypothesis, adhesion force measurements were performed by using AFM tips functionalized with hydrophilic molecules, which interact with the surfaces by means of hydrophilic/hydrophobic forces. In this context, hydrophilic surfaces apply large attraction forces to the tips, resulting into high adhesion force values.

Figure 1a shows histograms of the adhesion forces of nanocomposite films on silicon and glass substrates. The adhesion force values are lower when the tip interacts with the photopolymerized PS compared to the NRs since the first is more hydrophobic than the second (the WCA on pure films of PS and TiO<sub>2</sub> NRs are 95°±2° and 72°±2°, respectively, with the hydrophilic character of the NRs being attributed mainly to their surfactant-free areas). Figure 1a demonstrates that the adhesion force values are higher for samples on silicon (mean force ≈2.5 nN) compared to those on glass (mean force <0.5 nN). Therefore, we can assume that the NRs prefer to float on the surface of the nanocomposites prepared on silicon,

whereas they seem to prefer to lay closer to the glass substrate.

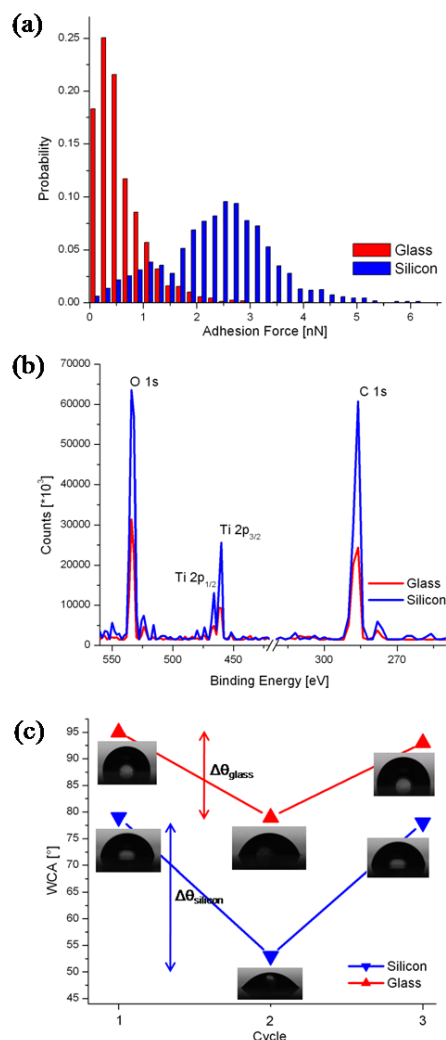


Figure 1: (a) Adhesion force peaks distribution in one-layer photopolymerized samples on silicon and glass substrates. (b) Normalized XPS spectra of one-layer photopolymerized samples on glass and silicon substrates.

(c) WCA measurements performed on one-layer photopolymerized nanocomposites on silicon and on glass substrates during a cycle of UV irradiation and vacuum storage, with the corresponding pictures of the water drops lying on the nanocomposite surfaces.

The different amount of NRs exposed at the surface of the films formed on the two different substrates has also been confirmed through XPS measurements. Figure 1b shows peaks typical for the TiO<sub>2</sub> [7, 8], i.e. the Ti 2p peak (which has two components, the Ti 2p<sub>1/2</sub> at 465 eV and the Ti 2p<sub>3/2</sub> at 460 eV) and the O 1s peak (at 530 eV), in addition to the C 1s peak (at 285 eV), which could be due to the presence of the polymer and of the oleic acid surfactant of the NRs. In particular, the two spectra presented in the figure have different intensities, depending on the number of NRs exposed on the surface of the examined samples [7].

In fact, the peaks have a higher intensity when silicon substrate is used, indicating a higher TiO<sub>2</sub> quantity on the sample surface, compared to samples prepared on glass.

Additionally, the water wettability measurements demonstrate how both the samples wetting properties and the variation of their WCAs is affected by the NRs distribution on the samples surface. Figure 1c illustrates the WCA values measured on photopolymerized films on glass and silicon substrates, (1) 48h after their photopolymerization, (2) after subsequent UV laser irradiation for 90 min, and (3) after 150h of vacuum storage. The nanocomposite films on silicon show an initial WCA of 79°±2°, quite lower than the one measured on photopolymerized PS films without NRs (95°±2°). On the other hand, when the samples are prepared on glass, they have an initial contact angle of 93°±2°, very similar to that of PS polymer without NRs. As mentioned above, the lower WCA value of samples on silicon compared to those on glass can be attributed to the higher number of hydrophilic TiO<sub>2</sub> NRs exposed on the surface of the formed nanocomposites, as already demonstrated by the AFM adhesion force and XPS measurements. The number of exposed NRs affects also the WCA values after UV irradiation. UV irradiation induces an increased hydrophilic character to the nanocomposites on both substrates (step 2 in Figure 1c). However, the decrease in the WCA is higher for the samples on silicon, with ΔWCA=26°, (WCA after UV becomes 53°±2°), compared to decrease for the samples on glass, which is ΔWCA=14°, (WCA after UV becomes 79°±2°). According to Caputo et al. [9], the TiO<sub>2</sub> NRs are responsible for the UV-induced hydrophilicity, through a mechanism that leads to increased degree of their surface hydroxylation. This explains why in the case of the samples on silicon, where the number of surface-exposed NRs is higher, the UV-induced WCA decrease is enhanced. Eventually, all nanocomposites completely recover their initial WCA after vacuum storage (step 3 in Figure 1c).

The difference in the surface content of TiO<sub>2</sub> NRs between films prepared on the two substrates can be attributed to the fact that glass and silicon exhibit different hydrophilicity. Particularly, glass is more hydrophilic than silicon, with measured values of WCA<sub>glass</sub>~40±1°, and WCA<sub>silicon</sub>~80±1° [10]. Since, as already mentioned above, the TiO<sub>2</sub> NRs have a more hydrophilic character than the styrene, they tend to interact better through polar forces with the glass than with silicon. As a consequence an increased number of NRs floats on the surface of the nanocomposites on silicon compared to those on glass, in agreement with the experimental findings.

### 3.2 Multi-Layer Nanocomposite Films

The addition of a second layer of photopolymerizable solution on a previously photopolymerized one, either on glass or silicon substrate, permits to switch the wetting characteristics of the previously prepared films. After the

completion of the photopolymerization of the second layer, the resulting samples have a total thickness of 950±50 nm.

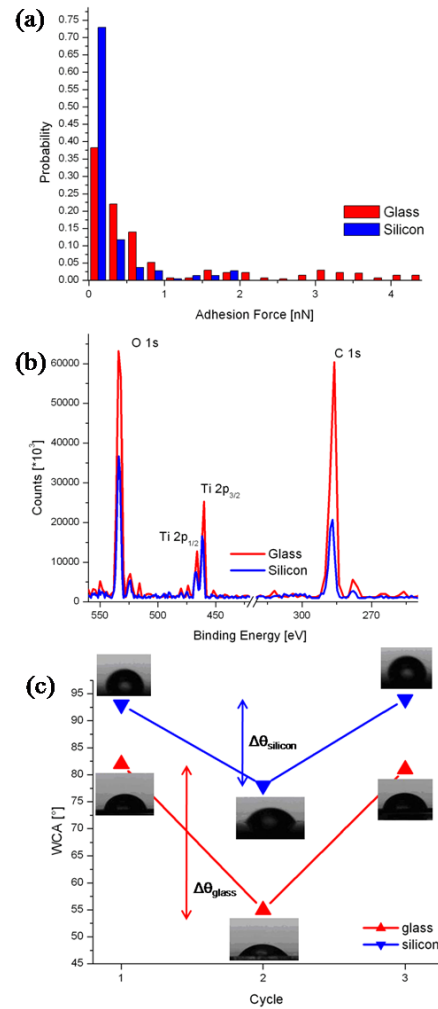


Figure 2: (a) Adhesion force peaks distribution in one-layer photopolymerized samples on silicon and glass substrates. (b) Normalized XPS spectra of two-layer photopolymerized samples on glass and silicon substrates. (c) WCA measurements performed on two-layer photopolymerized nanocomposites on silicon and on glass substrates during a cycle of UV irradiation and vacuum storage, with the corresponding pictures of the water drops lying on the nanocomposite surfaces.

Figure 2a shows the histograms of the adhesion forces of two-layer nanocomposites on silicon and glass substrates. In this case, the adhesion forces are higher for the samples on glass than for the samples on silicon. Therefore, we can assume that the NRs prefer to float onto the surface of the films on glass, whereas for nanocomposites prepared on silicon the NRs seem to stay close to the substrate. The finding is confirmed by the XPS measurements (Figure 2b) since the Ti 2p and O 1s peaks, characteristic for TiO<sub>2</sub>, have increased intensity for the two-layer samples prepared on glass compared to those prepared on silicon, confirming the

existence of a higher amount of NRs on the surface of former films.

Analogously, water wettability studies on these systems (Figure 2c) show that samples on glass have lower WCA values compared to those on silicon. In particular, the former present an initial contact angle value of  $82^{\circ} \pm 2^{\circ}$ , very similar to the one found for one-layer samples on silicon, and the latter show an initial contact angle value of  $95^{\circ} \pm 2^{\circ}$ , similar to the one found for one-layer samples on glass, clearly demonstrating the possibility to “swap” the wetting characteristics of the nanocomposites. Upon UV irradiation (step 2 Figure 2c) the hydrophilic character of the two-layer systems is, as expected, enhanced, with the enhancement being greater in the case of the samples on glass. Indeed, the UV-induced change of the WCA is  $\Delta WCA = 27^{\circ}$  for glass (post-irradiation  $WCA = 55^{\circ} \pm 2^{\circ}$ ) and  $\Delta WCA = 17^{\circ}$  for silicon (post irradiation  $WCA = 78 \pm 2^{\circ}$ ). The procedure is fully reversible and the initial wettability of the two-layer systems is fully recovered for both nanocomposites on glass and silicon after their storage in vacuum (step3 Figure 2c).

The increased number of TiO<sub>2</sub> NRs exposed onto the surface of the two-layer films prepared on glass with respect to those prepared on silicon can be explained assuming polar interactions between the NRs of the second deposited layer and the first photopolymerized one.

Therefore, the hydrophilic NRs of the second layer migrate close to the hydrophilic surface of the first nanocomposite layer on silicon, leaving the styrene molecules exposed on the surface. For the same reason the hydrophilic NRs float towards the surface when the second layer is deposited onto the hydrophobic first layer photopolymerized on glass.

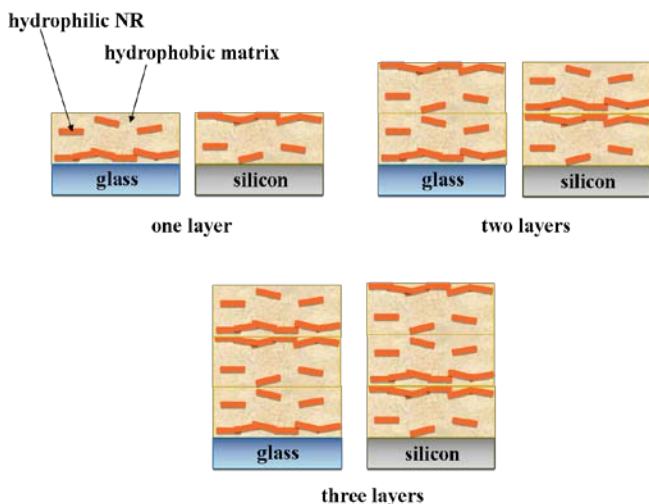


Figure 3: Schematization of the NRs distribution within the polymer matrix on one-layer, two-layer and three-layer samples on glass and silicon.

By adding and photopolymerizing successive layers on the previously deposited photopolymerized ones, the obtained WCA values continue to be reversed, leading to samples with higher hydrophilicity on silicon when an odd

number of layers is realized, whereas they have a higher hydrophilicity on glass when an even number of layers is realized (Figure 3).

## 4 CONCLUSIONS

Our results demonstrate the successful realization of photopolymerized nanocomposite films with tailored surface properties. We found that the substrate used and the number of layers realized influences the NRs distribution on the samples surface, thus modifying the surface wettability of the resulting materials. In particular, nanocomposites realized with an odd number of layers have a higher hydrophilicity when prepared on silicon compared to those prepared on glass. On the contrary, the realization of samples with an even number of layers result in a higher hydrophilicity when glass substrates are used compared to those prepared on silicon. In this way we demonstrate a strategy to swap the wettability characteristics of nanocomposite systems. Moreover, these systems show a reversible increase in their surface wettability upon UV irradiation and vacuum storage cycles. The possibility of easily realizing patterned nanocomposite films with tunable and highly controlled wettability characteristics, by using widely commercially available materials, opens up the way for the incorporation of these nanocomposites into specific parts of systems and devices, useful in biomedical and microfluidic applications.

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