

Switchable water absorption of paper via liquid flame spray nanoparticle coating

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Abstract Surface wetting/anti-wetting and liquid absorption are relevant properties of many porous solids including paper and other cellulose-based materials. Here we demonstrate how surface wetting by water and water absorption of commercially available kraft paper can be altered by thin nanoparticle coatings fabricated by liquid flame spray in facile and continuous one-step process. Surface wettability and absorption properties of paper increased with silica and decreased with titania (TiO₂) nanoparticle coatings. Moreover, the water-repellent (superhydrophobic) TiO₂ nanoparticle coated paper could be switched to superhydrophilic and water absorbing by

ultraviolet illumination. The experiments revealed that although surface wetting and liquid absorption of nanoparticle coated paper are strongly related to each other, they are two distinct phenomena which do not necessarily correlate. We propose wetting regimes on the nanoparticle coated paper samples on the basis of the experimental observations.

Keywords Wetting · Water absorption · Superhydrophobic · Cellulose · TiO₂ · Photoswitching

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Introduction

Utilization of cellulose-based materials, in which the main components are renewable, recyclable, and biodegradable, is one of the key issues in saving resources and achieving sustainable development. Therefore, economically viable paper, board, cotton fabrics, various cellulose-based composite materials, or highly porous superabsorbents and smooth and transparent films made of nanofibrillated cellulose are attractive material choices for many applications.

Cellulose is an abundant biopolymer available in plants and trees all over the world. Cellulose molecules readily create hydrogen bonds with water molecules, and thus cellulose is a hydrophilic and water absorbing material by nature (Eriksson et al. 2007; Kontturi et al. 2011). The great interaction between cellulose and water molecules is often a

desired property, and it can be utilized in, for example, absorbents to be used in diapers, filter papers, or paper-based microfluidic devices to transport the liquid in the device through capillary actions (Ballerini et al. 2012). However, the close interaction between cellulose and water molecules is not always a desired property of a material. For example, when paper gets wetted, the cellulose fibers swell and the bonds between individual fibers may weaken leading to a cohesive failure in the fiber network of paper. Or, waterproof clothing must be impermeable to liquid water, although permeation of moisture (gas) is often a desired property. To overcome the problems caused by wetting of cellulose-based materials, various hydrophobization treatments/barrier coatings have been developed, including surface sizing, extrusion coating, dispersion coating, chemical vapor deposition (CVD), and plasma deposition of fluoropolymer coatings (Mukhopadhyay et al. 2002; Kuusipalo 2008).

In the past few years, a wide range of extremely water-repellent, i.e., superhydrophobic, coatings have been developed on paper and cotton fabrics (Teisala et al. 2013b). Typically, water droplets cannot adhere to a superhydrophobic coating, but the droplets readily bounce or roll off the surface. Superhydrophobic properties, i.e., water contact angle $>150^\circ$, cannot be achieved on a smooth surface of any known solid. In addition to the chemical hydrophobicity, i.e., low energy surface chemistry, a superhydrophobic surface always needs to have sort of roughness or porosity on the scale of micrometers and below. Although for example paper is inherently rough and porous material, typically a sole hydrophobization treatment does not render its surface superhydrophobic, but in addition to the chemical modification, roughness of the surface needs to be increased (Mukhopadhyay et al. 2002; Balu et al. 2008).

Surface wetting, i.e., liquid spreading in the horizontal direction on the surface, is one of the fundamental parameters affecting the various finishing operations of paper, e.g. coating and printing (Kuusipalo 2008). Another important phenomenon, which is closely related to surface wetting and the various finishing operations of paper, is liquid absorption in the bulk of the paper. For example, in inkjet printing rapid drying and setting of aqueous inks are based on the rapid absorption of the ink vehicle in the porous substrate material (Swerin et al. 2008; Lamminmäki et al. 2011). On the other hand, in printed electronics excess ink penetration in the substrate needs to be

avoided to ensure precise quality of the printed patterns (Kordas et al. 2006; Bollström et al. 2009; Tobjörk and Österbacka 2011). Because penetration of, for example, ink or coating in the substrate affects material consumption, drying, setting, and adhesion, as well as appearance and functionality of the final product, it is of high interest to be able to control wetting and liquid absorption properties of paper.

To date, many detailed analyses of wetting properties of superhydrophobic coatings on paper have been reported (Teisala et al. 2013b). However, there are only few studies in which water absorption properties of superhydrophobic paper surfaces are discussed (Hu et al. 2009; Stanssens et al. 2011). Another extensively studied phenomenon is ultraviolet (UV) switchable wettability conversion on TiO_2 surfaces (Wang et al. 1997; Kanta et al. 2005; Fujishima et al. 2008) including TiO_2 coated paper (Stepien et al. 2012a, 2013b; Teisala et al. 2012b). However, UV-switchable water absorption in TiO_2 coated porous materials is only rarely reported. Apparently, there is only one previous study where UV-switchable water absorption on TiO_2 coated material was reported. In that study, Kettunen et al. (2011) demonstrated the use of TiO_2 coated nanocellulose aerogel membrane as a UV-switchable superabsorbent. Upon UV-illumination, the initially water-repellent aerogel membrane could absorb water 16 times its own weight. They anticipated photoswitchable water absorption to have good potential in microfluidic applications and porous TiO_2 coated materials with photocatalytic activity to open new possibilities in, for example, water and air purification.

We have recently demonstrated that surface wetting of paper and board can be controlled between superhydrophobicity (water contact angle $>150^\circ$) and superhydrophilicity (water contact angle $<10^\circ$) by continuous and one-step nanoparticle deposition method called liquid flame spray (LFS) (Teisala et al. 2010, 2013a; Stepien et al. 2011; Mäkelä et al. 2011). Here we focus on the other important phenomenon, i.e., water absorption in the porous surface of paper using LFS-coated commercially available kraft paper as a substrate material. Water absorption of the coated paper samples, both superhydrophobic titania (TiO_2) coated and superhydrophilic silica (SiO_2) coated, are studied and compared with the observed surface wetting. In addition, the inherently superhydrophilic SiO_2 coating is compared with the TiO_2

coating that has been switched to superhydrophilic by UV-illumination.

Materials and methods

Deposition of nanoparticle coatings

Machine glossed kraft paper (83 g/m², UPM-Kymmene) was used as a substrate for the water absorption experiments. The LFS nanoparticle coating procedure was carried out roll-to-roll at the Tampere University of Technology (TUT) on the Paper Converting and Packaging Technology (PCPT) pilot line in ambient conditions using the line speed of 50 m/min and precursor feed rate of 12 ml/min. Titanium tetraisopropoxide (TTIP, 97 % pure, Aldrich) was used as a precursor for the TiO₂ coating and tetraethyl orthosilicate (TEOS, 98 % pure, Aldrich) was used as a precursor for the SiO₂ coating. Both precursors were diluted in isopropanol with concentration of 50 mg (atomic metal)/ml. Hydrogen and oxygen with the ratio of 50/15 l/min were used as combustion gases in the process. Two alternative burner-to-substrate distances of 6 and 15 cm were used in deposition of the coatings. To investigate the influence of the thin nanoparticle coatings on water absorption of the paper, 3 different types of nanoparticle coatings (TiO₂, 6 cm; SiO₂, 6 cm; and SiO₂, 15 cm) were applied on the paper surface.

With the current processing parameters, the mean particle size is typically smaller than 20 nm in diameter, and the aggregated particles form a highly porous and transparent coating layer with thickness of few hundreds of nanometers (Teisala et al. 2012b; Stepień et al. 2013a). The SiO₂ nanoparticle coating fabricated by LFS creates a rough and high energy oxide surface, on which water droplets spread almost perfectly. When TiO₂ is used as a coating material, a carbonaceous overlayer spontaneously accumulates on TiO₂ nanoparticles during the LFS coating procedure of board and paper, and decreases surface energy of the rough oxide coating (Teisala et al. 2012b; Stepień et al. 2012a, b, 2013b; Aromaa et al. 2012; Teisala et al. 2013a). Therefore, the TiO₂ nanoparticle coated paper shows superhydrophobic properties with water contact angle greater than 160° and sliding angle of 10° for 10 µl droplets (Teisala et al. 2012a). Both the hydrophilic and hydrophobic nanoparticle coatings

can be fabricated in one-step coating process, where additional drying or curing steps are not needed. Detailed description and more information of the LFS roll-to-roll coating procedure can be found elsewhere (Teisala et al. 2010; Stepień et al. 2011; Mäkelä et al. 2011).

Water absorption (Cobb)

Water absorption of paper samples was measured using Cobb method according ASTM D 3285:99 and SFS-EN 20535:94 standards. The Cobb method is commonly used to measure water absorption of paper in industry. Briefly, the paper sample to be measured is weighed and mounted to the bottom of the Cobb vessel, after which the vessel is filled with certain amount of water. After the selected period of time, water is spilled off the vessel, the sample surface is dried between blotting papers, and the sample is weighed to measure how much water the sample absorbed through its surface during the selected period of time. The experiments were performed using custom-made rectangular Cobb vessel (2 × 3 cm), distilled water (~10 ml), and absorption time of 60 s (Cobb 60s). The given water absorption values are averages determined from three individual measurements. The given error margins indicate standard deviation.

Contact angle

Water contact angle experiments were performed in a conditioned room in ambient conditions of 23 °C/50 % relative humidity (RH) using distilled water and KSV CAM 200 equipment (KSV Instruments Oy, Finland). Contact angles were recorded 3 s after the droplet placement on the sample. The droplet volume in the contact angle measurements was fixed at 2 µl, and the given contact angle values are averages determined from five individual droplets. The given error margins indicate standard deviation.

Microscopy

Zeiss ULTRApplus field emission gun scanning electron microscope (FEG-SEM) was used for imaging the nanoparticle coated paper samples. Prior to the FEG-SEM imaging the samples were sputter coated with thin film of gold to obtain conductivity. The optical

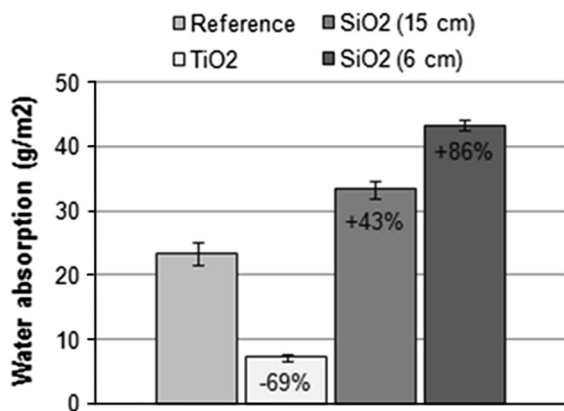


Fig. 1 Water absorption (Cobb 60 s) results of uncoated paper (reference) and TiO₂ and SiO₂ nanoparticle coated papers. Two burner-to-substrate distances, 15 and 6 cm, were used in deposition of the SiO₂ nanoparticle coatings

cross-section micrographs were captured using Zeiss Axioskop 40 microscope. The cross-section samples for the optical microscopy were cut with a microtome between supporting adhesive tapes.

UV-illumination

Ultraviolet-illumination was carried out with a lamp (Model UVG-54, UVP, USA) providing the central wavelength of 254 nm and illumination intensity of 2.25 mW/cm². The illumination was carried out in ambient laboratory conditions, and the subsequent water absorption and contact angle experiments were performed right after the samples were removed from the illumination to minimize the surface contamination and other possible changes occurring after the illumination.

Results and discussion

Our previous studies have shown that wettability of paper surface can be altered between superhydrophilicity and superhydrophobicity, i.e., between water contact angles of less than 10° and greater than 150°

Fig. 2 SEM micrographs of nanoparticle coated paper samples. **a** Uncoated paper, **b** TiO₂ coated paper (from distance of 6 cm), and **c** SiO₂ coated paper (from distance of 15 cm)

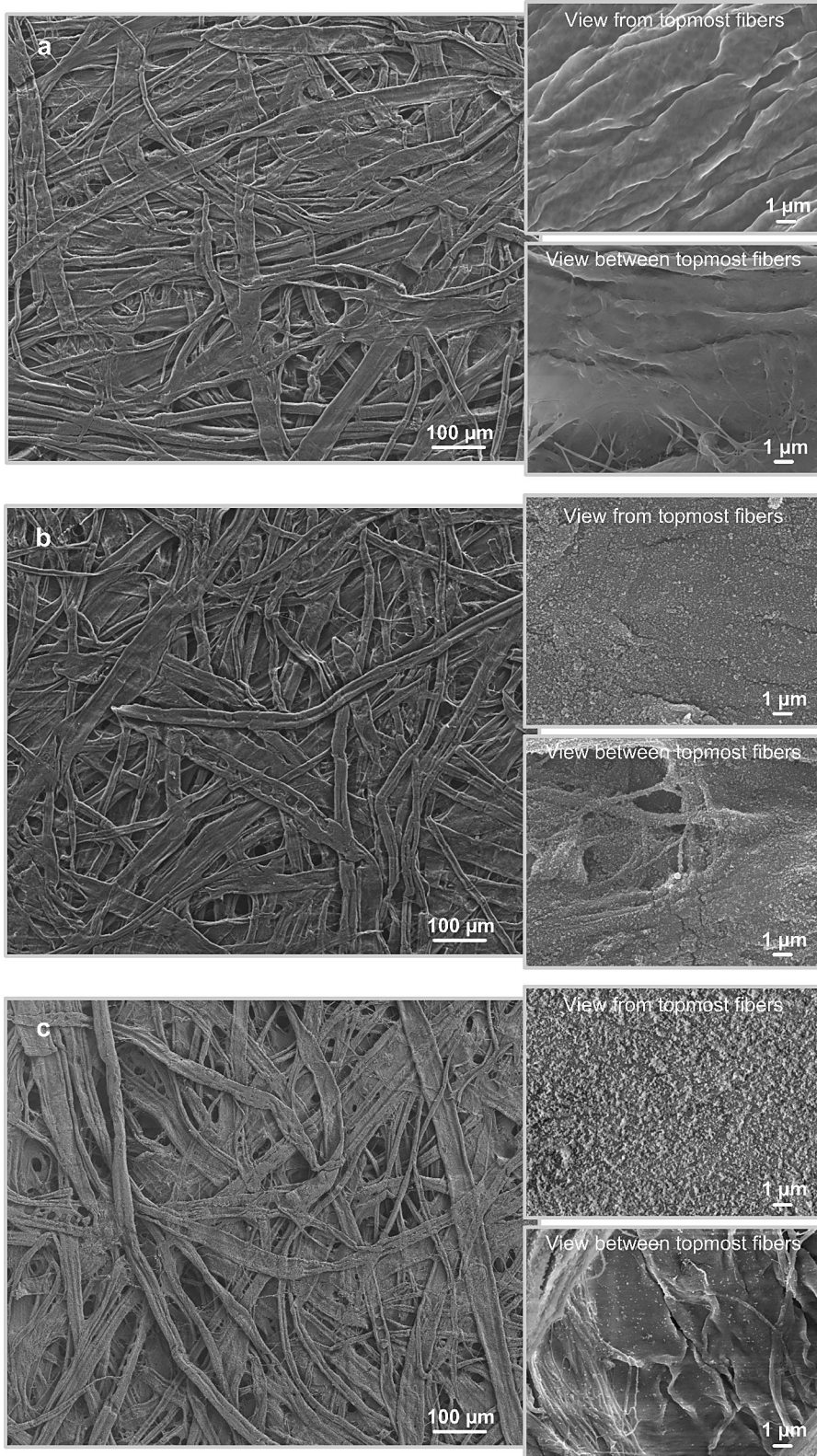
by thin nanoparticle coatings fabricated by LFS (Teisala et al. 2010, 2013a; Stepien et al. 2011; Mäkelä et al. 2011). The nanoparticle coating therefore determines capability of water to advance in the horizontal direction on the coated paper surface. However, the nanoparticle coatings not only determine the horizontal wettability of the coated paper surface, but also affect water penetration in the porous paper substrate. Figure 1 shows water absorption results (Cobb 60s) of the uncoated paper sample and nanoparticle coated samples. Water absorption in the paper was decreased by 69 % with the superhydrophobic TiO₂ coating, while the water absorption increased by 43 % (15 cm burner-to-substrate distance) and 86 % (6 cm burner-to-substrate distance) with the hydrophilic SiO₂ coatings.

Although wettability of paper surface can be considered as a surface phenomenon, while liquid absorption can be considered as a bulk phenomenon, still those two phenomena are closely connected to each other and cannot be completely separated. Table 1 reveals a decent correlation between water contact angle and water absorption on the nanoparticle coated paper surfaces. That is, a low water contact angle on the surface (good surface wettability) seems to predict high level of water absorption in the paper substrate: water contact angles of 6.4°, 10.5°, 119.5°, and 164.4° correspond to water absorptions of 43.3, 33.3, 23.3, and 7.2 g/m², respectively.

Both SiO₂ nanoparticle coatings, deposited either from the distance of 15 cm or from the distance of 6 cm, provide a good wettability for the paper surface with water contact angles of 10.5° and 6.4°, respectively (Table 1). Although a very good level of water spreading is achieved on both SiO₂ coated samples, there is still a notable difference in their water absorption capability. The SEM micrographs shown

Table 1 Water contact angle and water absorption of nanoparticle coated paper samples

| | Uncoated | TiO ₂ coated | SiO ₂ coated, 15 cm | SiO ₂ coated, 6 cm |
|--------------------------------|-------------|-------------------------|--------------------------------|-------------------------------|
| Contact angle (°) | 119.5 ± 1.0 | 164.4 ± 0.9 | 10.5 ± 1.0 | 6.4 ± 1.2 |
| Absorption (g/m ²) | 23.3 ± 1.7 | 7.2 ± 0.5 | 33.3 ± 1.4 | 43.3 ± 0.8 |



in Fig. 2 give explanation for the observed different wettability and water absorption of the two SiO₂ coated samples. With the coating deposition distance of 15 cm (Fig. 2c), the nanoparticle coating exists mainly on the topmost fibers of the paper surface, and

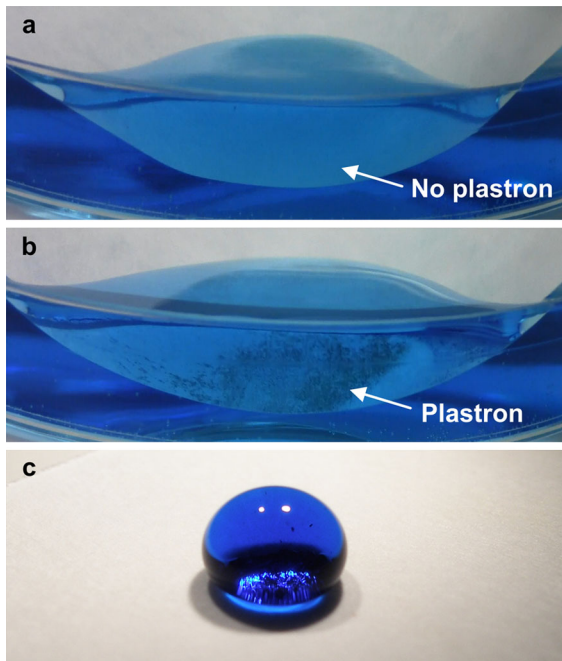


Fig. 3 Plastron layer on superhydrophobic TiO₂ nanoparticle coated paper. **a** Paper without the nanoparticle coating submerged in methylene blue colored water, **b** superhydrophobic nanoparticle coated paper submerged in the colored water, and **c** colored water droplet sitting on the coated paper surface

the fibers beneath them remain practically uncoated. In contrast, with the coating deposition distance of 6 cm (Fig. 2b), also the fibers beneath the topmost fibers get covered with the nanoparticle coating. That is, in both cases regardless of the coating deposition distance water advances easily on the hydrophilic SiO₂ nanoparticle coating on the topmost fibers of the paper substrate. However, when the hydrophilic SiO₂ nanoparticle coating exists also on the fibers beneath the topmost fiber layer, water is attracted to penetrate more efficiently between the fibers in the bulk of the paper, and thus water absorption capability of the paper is further increased.

The superhydrophobic TiO₂ nanoparticle coating reduces water absorption of paper by entrapping air between the protrusions on the surface. As a consequence, a liquid-solid-air composite interface is formed on the coating surface, which is the basis of the phenomenon of superhydrophobicity. The layer of air existing on the rough surface of TiO₂ nanoparticle coating, i.e., so-called plastron layer (Jin et al. 2011; Verho et al. 2012), can be seen in Fig. 3 on the nanoparticle coated paper submerged in colored water (video available in Online Resource 1) and below a colored water droplet sitting on the nanoparticle coated paper.

Figure 4 shows shape of methylene blue colored water droplets (~20 μl) placed on the nanoparticle coated paper samples (upper row) and the color traces left on the surfaces after the droplets were removed with a blotting paper (lower row). The partial color trace on the TiO₂ nanoparticle coated paper sample

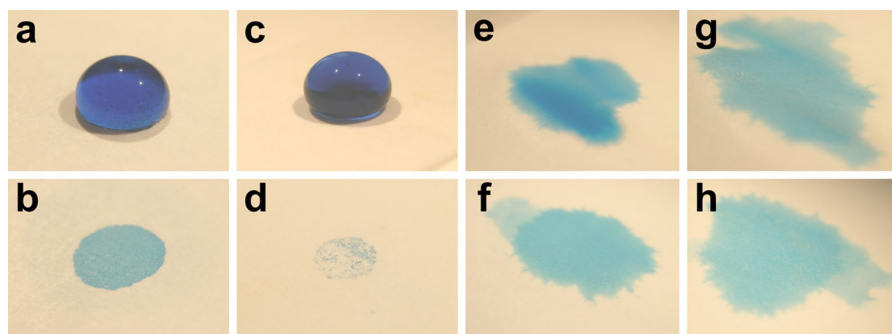


Fig. 4 Photographs of methylene blue colored water droplets on nanoparticle coated paper samples and the color traces left on the surfaces after the droplets were removed. *Upper row* droplets lying on the samples after 60 s from the droplet placement. *Lower row* the color traces left on the surfaces after

the droplets were removed with a blotting paper. **(a, b)** Uncoated paper, **(c, d)** TiO₂ coated paper, **(e, f)** SiO₂ coated paper with burner-to-substrate distance of 15 cm, and **(g, h)** SiO₂ coated paper with burner-to-substrate distance of 6 cm. Images are not in scale

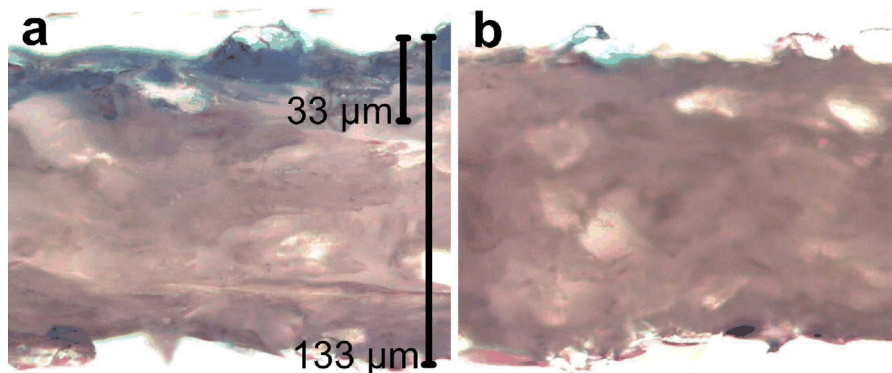


Fig. 5 Optical micrographs of methylene blue color traces on paper samples. Side view images of **a** uncoated paper and **b** TiO₂ nanoparticle coated paper

Table 2 Water contact angle and water absorption of TiO₂ nanoparticle coated paper upon UV-illumination ($\lambda = 254$ nm)

| | TiO ₂ , no UV | TiO ₂ , 15 min UV | TiO ₂ , 1 h UV | TiO ₂ , 3 h UV |
|--------------------------------|--------------------------|------------------------------|---------------------------|---------------------------|
| Contact angle (°) | 164.4 ± 0.9 | 68.0 ± 1.5 | 22.5 ± 2.0 | 7.9 ± 0.5 |
| Absorption (g/m ²) | 7.2 ± 0.5 | 27.1 ± 2.6 | 25.7 ± 2.6 | 27.8 ± 1.3 |

reveals that a large amount of entrapped air existed below the droplet on the surface (Fig. 4c, d). Optical micrograph side view images of the color traces on the uncoated and TiO₂ nanoparticle coated paper samples (Fig. 5) indicate that the colored water was capable of penetrating at least to the depth of approximately 30–35 μm on the uncoated paper, while on the TiO₂ coated paper a weak color trace can be detected only on the topmost areas of the sample surface. Any noticeable difference in the penetration depth between the uncoated paper and SiO₂ nanoparticle coated paper samples could not be detected.

Previous studies on superhydrophobic TiO₂ nanoparticle coatings fabricated by LFS have revealed that a wettability conversion can be initiated on the photocatalyst surface by UV-illumination (Stepien et al. 2012a, 2013b; Teisala et al. 2012b). That is, the superhydrophobic coating can be switched to superhydrophilic by altering its surface chemistry through decomposition of the thin low energy carbonaceous overlayer on top of the high energy oxide coating. Although the earlier experiments indicate the removal of carbonaceous material from the coating surface to be the most important single factor explaining the UV-initiated wettability conversion on the TiO₂ nanoparticle coated paper, the other possible photoreactions

occurring on the surface cannot be completely ruled out (Teisala et al. 2012b).

Table 2 shows the changes in water contact angle and water absorption capability of the TiO₂ nanoparticle coated paper after different periods of UV-illumination ($\lambda = 254$ nm). Already after 15 min of UV-exposure, water contact angle on the sample had decreased from its initial state of 164.4° to 68.0°. After 3 h of illumination, the surface had reached almost perfect wettability, and water contact angle on the sample was measured to be less than 8°. As was expected, the UV-illumination also increased water absorption capability of the TiO₂ nanoparticle coated paper sample. Interestingly, water absorption of the sample saturated at ~ 27 g/m² already after 15 min of illumination. That is, although water contact angle on the surface still continued a drastic decrease with the extended illumination, water absorption capability of the sample no longer increased. Another important observation is the fact, that although the surface of the TiO₂ nanoparticle coated paper experienced almost perfect wettability with water contact angle of 7.9° upon UV-illumination of 3 h, its water absorption capability was increased only by 19 % compared to the uncoated paper sample. In comparison, the SiO₂ nanoparticle coatings could improve water absorption

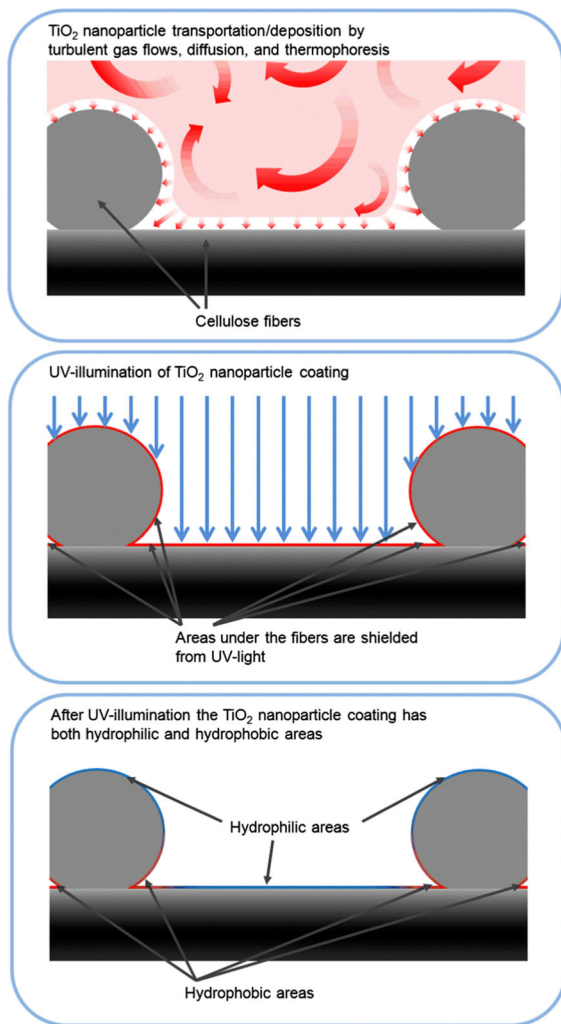


Fig. 6 Simplified illustration of hydrophobic TiO_2 nanoparticle coating deposition on paper substrate and formation of hydrophilic areas on the topmost fiber layers of the coated surface upon UV-illumination. *Upper row* particle transportation by gas flows, diffusion, and thermophoresis yield to coating deposition also below the topmost fibers of the paper substrate. *Middle* due to good UV-absorption properties of TiO_2 , scattering of UV-light on the surface is reduced, and it is likely that UV-light cannot reach all the coated areas below the fibers. *Lower row* upon UV-illumination the coating has both hydrophilic and hydrophobic areas. Images are not in scale

of paper by 43 % (15 cm burner-to-substrate distance) and 86 % (6 cm burner-to-substrate distance).

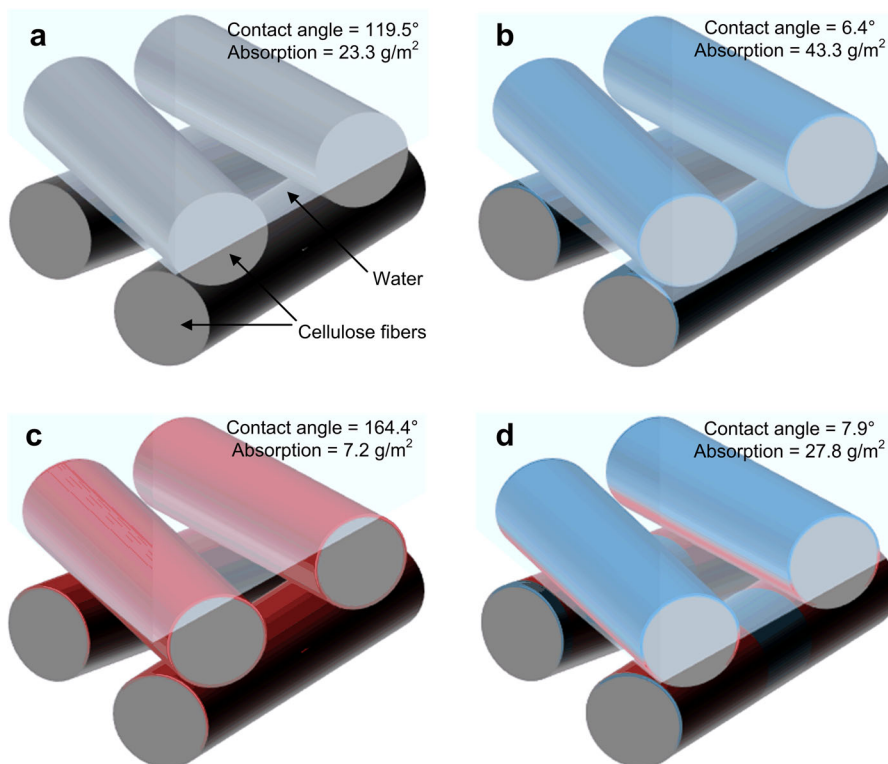
The independence between water contact angle and water absorption of the nanoparticle coated paper samples reveals that although the surface wetting and water absorption of paper are strongly related to each other and cannot be completely separated, they are two

distinct phenomena which do not necessarily correlate. Although water spreading on the nanoparticle coated paper surface can occur almost perfectly along the hydrophilic coating on topmost fibers of the paper substrate, existence of any hydrophobic coating below the topmost areas of the fibers can hinder water penetration in the bulk of the paper. We assume that some areas of the nanoparticle coating, which were screened by above TiO_2 nanoparticle layers or the fibers of the paper during the UV-illumination, partially maintain their hydrophobic character (Fig. 6) and thus hinder water penetration in the paper substrate. The above conclusion is supported by our earlier studies, in which surface chemical analyzes on the LFS nanoparticle coated board samples were executed. The earlier studies consistently show that even after photodegradation of the carbonaceous material and related superhydrophilicity conversion on TiO_2 (Stepien et al. 2012a; Teisala et al. 2012b), the amount of carbonaceous material on the TiO_2 nanoparticle coating still remains higher compared to that on the initially hydrophilic SiO_2 nanoparticle coating (Stepien et al. 2012b; Teisala et al. 2013a).

Different wetting states on the nanoparticle coated paper samples are proposed in Fig. 7, where blue color corresponds to superhydrophilic nanoparticle coating on fibers of the paper substrate and red color corresponds to superhydrophobic nanoparticle coating on the fibers. Figure 7a illustrates a moderate water penetration on the uncoated paper surface, while Fig. 7b, c illustrate enhanced and prevented water penetration in the paper substrate on the SiO_2 and TiO_2 nanoparticle coated samples, respectively. Figure 7d illustrates a moderate water penetration on the UV-illuminated superhydrophilic TiO_2 nanoparticle coated sample, where hydrophobic areas below the topmost fibers are expected to hinder water penetration in the substrate.

When the average diameter of an individual fiber on the paper surface is considered to be around $50\ \mu\text{m}$ and the porosity of the paper surface is considered to be around 70 %, the mass of water penetrated in the paper is equal to the measured water absorption values if water would penetrate in the depth of $\sim 33\ \mu\text{m}$ on the uncoated paper sample, $\sim 62\ \mu\text{m}$ on the SiO_2 nanoparticle coated paper sample, $\sim 10\ \mu\text{m}$ on the TiO_2 nanoparticle coated paper sample, and $\sim 40\ \mu\text{m}$ on the UV-illuminated TiO_2 nanoparticle coated paper sample. Although a direct comparison cannot be done,

Fig. 7 Proposed wetting of nanoparticle coated paper samples. **a** Uncoated paper, **b** SiO₂ nanoparticle coated paper, **c** TiO₂ nanoparticle coated paper, and **d** TiO₂ nanoparticle coated paper upon UV-illumination. *Blue color* refers to superhydrophilic nanoparticle coating and *red color* refers to superhydrophobic nanoparticle coating. (Color figure online)



the scheme proposed in Fig. 7 and the measured water absorption values are in the same range and good consensus with each other.

Conclusions

Water absorption capability of LFS-coated paper samples was examined. The superhydrophilic SiO₂ nanoparticle coating could increase water absorption of paper by 86 %, while the superhydrophobic TiO₂ nanoparticle coating decreased water absorption of paper by 69 %. The superhydrophobic TiO₂ nanoparticle coated paper could be switched to superhydrophilic and water absorbing by UV-illumination. Water absorption of the UV-illuminated sample saturated at 19 % greater level compared to the uncoated paper sample already after a short period of UV-illumination, while a drastic water contact angle decrement still continued on the sample with extended UV-illumination. That is, although surface wetting and water absorption of paper are strongly related to each other, they are two distinct phenomena that do not necessarily correlate. Wetting of paper surface by

water is sensitive to changes on the topmost areas of the fibers, while water absorption capability of paper is more a bulk phenomenon. On the basis of the experimental results, a scheme of wetting regimes on the nanoparticle coated paper samples was proposed.

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