ToF-SIMS Analysis of UV-Switchable TiO₂-Nanoparticle-Coated Paper Surface

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ABSTRACT: The chemical composition of a TiO₂ nanoparticle coated paper surface was analyzed using time-of-flight secondary ion mass spectrometry (ToF-SIMS) to study the interconnection between wettability and surface chemistry on the nanoscale. In this work, a superhydrophobic TiO₂ surface rich in carboxyl-terminated molecules was created by a liquid flame spray process. The TiO₂ nanoparticle coated paper surface can be converted by photocatalytic oxidation into a highly hydrophilic one. Interestingly, the hydrophilic surface can be converted back into a superhydrophobic surface by heat treatment. The results showed that both ultraviolet A (UVA) and oven treatment induce changes in the surface chemistry within a few nanometers of the paper surface. These findings are consistent with those from our previously reported X-ray photoelectron spectroscopy (XPS) analysis, but the ToF-SIMS analysis yields more accurate insight into the surface chemistry.

1. INTRODUCTION

Nanoparticles are frequently used to create functional surfaces. Different types of nanoparticles have been applied to form surfaces with versatile wetting properties, such as the ability to be transformed from hydrophobic to hydrophilic, and vice versa.^{1,2} The importance of such surface arises because wettability has an effect on material performance^{3–5} in, for example, printing. In this work, a superhydrophobic paper surface was created by deposition of TiO₂ nanoparticles on coated paper using a liquid flame spray (LFS) process.^{6,7} This roll-to-roll process, which is performed at high speeds, is a promising technology for producing new paper-based products with innovative functionalities.^{8,9} The LFS process can also be used to create a broad spectrum of inorganic oxide nanoparticles, including Al₂O₃, ZrO₂, Mn₂O₃, and Fe₂O₃.^{7,10–13}

It has been shown that changes in the wetting properties are related to the surface chemistry and surface morphology induced by the nanoparticle layer.^{8,9} Typically, changes in the surface properties are caused by external factors such as temperature,^{14,15} solvent,¹⁶ electric potential,¹⁷ light,^{15,18} or mechanical stress.¹⁹ Since nanoparticles can be modified, it is important to establish a connection between their chemistry and surface wettability. The material studied here, TiO₂, can be activated by ultraviolet light, an important property that has

attracted attention due to the large range of potential applications: photoactivated TiO₂ nanoparticles can be used for the degradation of environmental pollution, self-cleaning glass, or the recovery of metal cations.²⁰

Photocatalytic wettability conversion between the hydrophobic and hydrophilic states of TiO₂ has also been reported.^{15,17,21,22} These two opposite states can be achieved using different TiO₂ nanoparticle coating treatments. Here a hydrophobic surface is created by the LFS process on paper substrate. Highly hydrophilic TiO₂ films can then be generated by UV irradiation;³ the recovery of surface hydrophobicity occurs under ambient conditions in dark,¹⁸ and the change can be accelerated by heat treatment.^{4,23} Clearly, the surface chemistry of the substrate significantly affects these types of processes. Our previous study²⁴ showed that TiO₂ nanoparticle deposition leads to superhydrophobicity only on paper or paperboard surfaces, whereas deposition on inorganic substrates such as glass, copper, aluminum, or stainless steel results in hydrophilicity. This is due to the high-temperature LFS process that creates a hydrocarbon-rich

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layer on top of TiO₂ nanoparticles when deposited on paper or paperboard.

The chemical composition of the sample surface determines the interactions occurring on the substrate. It has been shown²⁵ that a thin layer on the surface can have characteristics that are generally not observed in the bulk material. In the case of paper-based samples, surface analysis becomes complicated since the paper and the paper coatings exhibit significant heterogeneity in terms of both chemistry and morphology. Hence, accurate analytical methods with adequate molecular sensitivity are necessary for understanding the surface chemistry.^{26,27}

Time-of-flight secondary ion mass spectrometry (ToF-SIMS) is an analytical technique that can be applied in surface-sensitive studies of a wide range of samples. The extraction of positive and negative secondary ions from the surface at depths in the range of 1 nm and with a lateral resolution of 200 nm²⁶ provides detailed information about highly characteristic material-specific chemical structures in the form of a mass spectrum.^{28,29} On the basis of ToF-SIMS spectra, the relationships among typical fragmentation patterns for known chemical structures can be used to distinguish different functional groups such as OH, COOH, CO₃, CO₂CH₃, and SO₄H.^{30,31} An advantage of ToF-SIMS is the parallel high sensitivity detection of all masses, which is useful for imaging and ideal for visualizing the heterogeneity of the sample surface. Electrical insulators such as paper, fibers, or polymers can be measured by minimizing differential charging. This makes ToF-SIMS surface mapping especially important for analysis of molecular monolayer films and organized assemblies, both of which have potential applications in sensors, the self-deposition of polymers and proteins, and wetting and adhesion studies.^{28,32,33} Nevertheless, ToF-SIMS is vulnerable to topographic and contamination effects, which increase the amount of information collected, making the comparison and interpretation of data difficult.

The present work uses ToF-SIMS to achieve more accurate chemical characterization of the chemical changes occurring during ultraviolet A (UVA) irradiation and heat treatment of initially superhydrophobic TiO₂ nanocoated paper surfaces. The authors' previous X-ray photoelectron spectroscopy (XPS) study³⁴ showed that UVA irradiation induces photocatalytic oxidation of the TiO₂ surfaces and hence high hydrophilicity. The subsequent loss of hydrophilicity is related to a decrease in the amount of oxygen associated with hydroxyl groups and an increase in the amount of oxygen related to carboxyl groups. The carboxylic groups are thought to originate from atmospheric contamination or volatile organic compounds in the paperboard. However, there was some uncertainty about the exact chemical composition of the outermost layer because the XPS sampling depth is greater (approximately 10 nm) than that of ToF-SIMS. The use of ToF-SIMS makes it possible to obtain more detailed information about the surface chemical composition. Section 2 describes the materials and methods used in the study, and Section 3 summarizes the main surface chemistry results from contact angle (CA) and ToF-SIMS analyses. The results are discussed in Section 4, and the conclusions are presented in Section 5.

2. MATERIALS AND METHODS

2.1. Substrates. A standard 83 g/m² base paper (Stora Enso, Sweden) was blade coated in a minipilot-scale roll-to-roll coater (Rotary Koater, RK Print Coat Instruments, UK).

The coating color recipe contained 100% of kaolin (Capim SP, Imerys, UK) and 10 pph of latex (DL 1066, Dow Chemicals, Switzerland) with a target coat weight of 20 g/m². The coating color was formulated to be as simple as possible, with known chemical constituents that are readily identifiable in spectroscopic analyses. An LFS technique was used to deposit TiO₂ nanoparticles on the pigment coated paper. Nanoparticle deposition was carried out in a continuous roll-to-roll process at a constant web speed of 50 m/min under ambient conditions. The liquid precursor, titanium(IV) isopropoxide (TTIP, Aldrich, Germany), dissolved in isopropanol (IPA) with an atomic titanium concentration of 50.0 mg/mL, was fed into a nozzle at a rate of 32.0 mL/min. The distance between the nozzle and the paper substrate was 15 cm. For details about the LFS nanodeposition process, see refs 8, 35, and 36.

2.2. Sample Preparation. The TiO₂-nanocoated surface was exposed to UVA light (Bluepoint 4 ecocure, Hönle UV Technology, Germany) at a central wave-length of 365 nm, with a 320–390 nm filter. Irradiation at a constant intensity of 50 mW/cm² for 30 min induced a change in the surface properties from superhydrophobic to hydrophilic. To recover the initial hydrophobicity, the samples were placed in an oven at 150 °C for 3 min. The UVA irradiation and heat treatment time periods were chosen based on previous experiments.³⁴

Figure 1. Wettability conversion of TiO₂ nanocoated paper.

Figure 2. ToF-SIMS images of total ion counts in positive ion mode for the TiO₂ nanocoated paper (upper row) and the reference paper (lower row).

Figure 3. ToF-SIMS positive ion spectra of the paper coating components on the reference paper and the TiO₂ nanocoated paper for (a) $m/z = 0\text{--}100$ Da and (b) $m/z = 100\text{--}600$ Da.

In aspect of a time used for a recovery of hydrophobicity, these are the most efficient parameters. Our other studies reported by Teisala et al.³⁷ show how different oven temperatures affect the recovery rate.

The samples were also partially covered with a photomask to allow only selective exposure to the UVA irradiation with the formation of sharp boundaries around the exposed areas. In this way, four different types of samples were produced: untreated reference samples, UVA exposed samples, oven-treated non UVA exposed samples, and oven-treated UVA exposed samples. Similar sets of samples were prepared for plain coated paper and for coated paper with TiO₂ nanoparticles. All the experiments were carried out under ambient conditions.

2.3. Surface Characterization. CA measurements were performed using a sessile drop method. Static contact angles were measured using a contact angle goniometer, (KSV CAM 200, KSV Instruments Ltd., Finland) with an automatic dispenser and a motorized stage. The tests were performed by dispensing purified (Milli-Q filtration unit, Millipore, U.S.A.; resistivity 18.2 MΩ)

Table 1. Ion Fragments and Structural Assignments for Hydrocarbon Fragments^{29,39}

hydrocarbon type	m/z	secondary ion structure
$C_nH_{2n+1}^+$	29	$(C_2H_5^+)$
	43	$(C_3H_7^+)$
	57	$(C_4H_9^+)$
$C_nH_{2n-1}^+$	41	$(C_3H_5^+)$
	55	$(C_4H_7^+)$
	69	$(C_5H_9^+)$
$C_nH_{2n-3}^+$	39	$(C_3H_3^+)$
	53	$(C_4H_5^+)$
	67	$(C_5H_7^+)$

water droplets with a volume of approximately 2.0 μL . Each result is an average of at least three determinations for a sample measured in air under ambient conditions (room temperature (RT) $23\text{ }^\circ\text{C} \pm 1\text{ }^\circ\text{C}$, and relative humidity (RH) $30 \pm 5\%$). The images were analyzed using a software that uses a Laplacian fit to the projected droplet curvature.

The surface chemistry was investigated using ToF-SIMS, which provides molecular-level information at high spatial resolution. With an imaging depth of 1 nm, it is well suited to imaging the distribution of individual molecules on the outermost surface.³⁸ The ToF-SIMS experiments were performed with a PHI TRIFT II (USA) equipped with a pulsed liquid metal ion gun. Spectra were acquired in positive ion mode over the mass range of 2–2000 Da (Da) using a Ga⁺ primary source with a 100 × 100 μm² raster size, a 15 kV applied voltage, a 600 pA aperture current, and a 10 min acquisition time. A low electron energy flood gun was used to prevent sample surface charging. Images were collected over a 2 × 2 mm² area in non-interlaced mode, i.e., with analysis and sputtering active in different ToF cycles. At least three different spots on each sample were analyzed, and the most representative were presented. The mass spectra were calibrated based on reference peaks such as CH₃⁺, C₂H₃⁺, and C₃H₅⁺. Relative normalized intensities were determined by dividing each peak of the spectrum by the total measured intensity.

3. RESULTS

3.1. Contact Angle. A superhydrophobic paper surface was created by deposition of TiO₂ nanoparticles on a paper substrate. Figure 1 shows the changes in the water CA values for TiO₂ nanoparticle coated paper after 30 min of UVA exposure and 3 min of oven treatment. It can be observed that an initially superhydrophobic surface with a water CA of 161° can be converted into a superhydrophilic surface with a water CA of less than 10° by exposure to UVA light. Placing the sample in an oven at 150 °C for 3 min restored the surface superhydrophobicity. The same procedure was repeated for the reference coated paper (without TiO₂ nanoparticles). In this case, the CAs ranged from 77° for a sample before treatment to 61° after UVA irradiation and 79° after oven treatment.

3.2. ToF-SIMS Characterization. ToF-SIMS mapping of the paper samples was used to evaluate the changes caused by both UVA and oven-treatment. Figure 2 shows images of a TiO₂ nanocoated paper and a reference paper. Masks were used to create regions subjected to different treatments: before treatment (Figure 2a,e), after UVA irradiation (Figure 2b,f), after UVA irradiation with subsequent oven treatment (Figure 2c,g), and oven treatment only (Figure 2d,h). It was found that, for the TiO₂ nanocoated paper samples (Figure 2, upper row), each treatment produced changes in the total ion count; however, these were not observed for the reference paper (Figure 2, lower row). To explain these differences, further analyses were performed, including evaluation of spectra from each region.

Traditional paper grades contain numerous organic components that typically are used in coating formulations, and this makes it difficult to identify the chemical properties of the surface directly. For this study, using a known coating recipe, we produced a coated paper that served as a reference paper. Then, applying the LFS process, TiO₂ nanoparticles were deposited on the coated paper. Chemical characterization was performed based on the positive ion ToF-SIMS spectra of the components of the coating color, the reference paper, and the TiO₂ nanocoated paper (Figure 3a,b). Between 0 and 100 Da, the spectra are dominated by the typical peaks related to metals at $m/z = 23$ (Na⁺), 27 (Al⁺), 28 (Si⁺), and also by hydrocarbon fragments of type C_{*n*}H_{2*n*+1}⁺, C_{*n*}H_{2*n*-1}⁺ and C_{*n*}H_{2*n*-3}⁺. Examples of such hydrocarbon fragments are presented in Table 1.

Between 100 and 300 Da, peaks were detected at $m/z = 115$, 149, 173, 249, 301, and 442. These originate from derivatives of

hydrocarbon chains and oxygenated molecules containing Al⁺ and Si⁺, for example, C₂₄O₆H₃SiAl⁺. The latex used in the coatings was identified as styrene butadiene latex. The typical positive peaks of polybutadiene and polystyrene are shown in Table 2.

Table 2. Ion Fragments and Structural Assignments for Positive Ions Characteristic of Polybutadiene and Polystyrene^{29,39}

	m/z	secondary ion structure
Polybutadiene	27	(C ₂ H ₃ ⁺)
	39	(C ₃ H ₃ ⁺)
	41	(C ₃ H ₅ ⁺)
	55	(C ₄ H ₇ ⁺)
	67	(C ₅ H ₉ ⁺)
Polystyrene	77	(C ₆ H ₅ ⁺)
	91	(C ₇ H ₇ ⁺)
	103	(C ₈ H ₇ ⁺)
	105	(C ₈ H ₉ ⁺)
	115	(C ₉ H ₇ ⁺)
	117	(C ₉ H ₉ ⁺)
	128	(C ₁₀ H ₈ ⁺)
	141	(C ₁₁ H ₉ ⁺)
	152	(C ₁₂ H ₈ ⁺)
	165	(C ₁₃ H ₉ ⁺)
	178	(C ₁₄ H ₁₀ ⁺)
	193	(C ₁₅ H ₁₃ ⁺)

The spectra show peaks at $m/z = 27$ (C₂H₃⁺), 39 (C₃H₃⁺), 41 (C₃H₅⁺), 55 (C₄H₇⁺), 77 (C₆H₅⁺), 91 (C₇H₇⁺), 105 (C₈H₉⁺), 115 (C₉H₇⁺), and 165 (C₁₃H₉⁺) corresponding to ions typically associated with the fragmentation products of this type of latex. Spectra for different coating color components were collected, making it possible to identify them in the paper sample spectra. As expected, the reference paper spectrum contains peaks characteristic of kaolin and latex particles with fragments of hydrocarbons and high molecular weight additives. The spectrum of TiO₂ nanocoated paper, in addition to containing these same peaks, is dominated by Ti⁴⁺ at $m/z = 48$. Other peaks are related to titanium isotopes and protonated ions such as TiH⁺ at $m/z = 49$, 50, and TiOH⁺ at $m/z = 64$, 65.^{31,40,41} Peaks identified as hydrocarbon chains such as C_{*n*}H_{2*n*+1}⁺, C_{*n*}H_{2*n*-1}⁺, latex, and/or oxygen-containing species are present at $m/z = 27$, 41, 55, 77, 91, 105, 115, 129, and 165. The negative ion spectra for untreated TiO₂ nanocoated paper are dominated by the O⁻ and OH⁻ ions typical of hydroxylated titanium oxides surfaces.³¹

The changes caused by UVA irradiation and oven treatment of TiO₂ nanocoated papers were detected mainly in the positive ion spectra. Figure 4a,b shows spectra over the range 0–100 Da and over the range 100–300 Da, respectively, for TiO₂ nanoparticle-coated paper subjected to different treatments: untreated, UVA irradiated, UVA irradiated and subsequently oven treated, and oven treated only. The spectra show strong signals for the Ti⁴⁺ related peaks at $m/z = 47$, 48, and 49 (the peak at $m/z = 23$ related to Na⁺ can be ignored); similar series corresponding to TiO⁺ and TiO₂⁺ have also been detected.^{31,40,41} The results show that the hydrocarbon peaks at $m/z = 41$, 43, 55, 77, 91, 105, 115, 129, and 165 decrease sharply after UVA irradiation; in contrast, after UVA and subsequent oven treatment, the same peak patterns increase.

Figure 4. Positive ion spectra of TiO_2 nanocoated paper before treatment and after three different surface treatments: UVA irradiation, UVA irradiation with subsequent oven treatment, and oven treatment only for (a) $m/z = 0\text{--}100$ Da and (b) $m/z = 100\text{--}300$ Da.

The spectra for the reference paper were collected for comparison. Figure 5a,b shows positive ion spectra over the range 0–100 Da and over the range 100–300 Da, respectively, for similar sets of samples, without TiO_2 nanoparticles. Characteristic peak patterns are visible, corresponding to kaolin with $m/z = 27$ and 28; latex with $m/z = 91$, 105, and 165; and hydrocarbons such as $\text{C}_n\text{H}_{2n+1}^+$ and $\text{C}_n\text{H}_{2n-1}^+$. The findings were nearly identical for all the samples, with minimal differences in their relative intensities, which were higher after oven treatment.

Figure 6 shows the normalized relative intensities of hydrocarbon fragments from the TiO_2 -nanocoated paper. The critical differences between the spectra appear after UVA irradiation: all the relative intensities decreased. By contrast, oven treatment increased the relative intensities of the hydrocarbon ions at $m/z = 13$, 15, 27, 28, 29, 39, 41, 43, 55, and 57 to the initial levels, but even greater increases were observed for the hydrocarbon ions at $m/z = 67$, 77, 81, 91, 105, 115, 128,

141, and 165. The second group of hydrocarbons are associated with fragmentation products of the latex. The same procedure was performed for the reference papers, and the results are presented in Figure 7. The characteristic peaks were identical, and no significant changes were observed in the relative intensities after UVA irradiation. Nevertheless, oven treatment increased the relative intensities of all these peaks in the same way as for the TiO_2 nanocoated paper. Furthermore, the peak intensities for the second group of hydrocarbons increased to even higher levels; for example, the relative intensity of the peak at $m/z = 91$ doubled after oven treatment.

Some of the peaks from the ToF-SIMS positive ion spectra were analyzed separately. Figure 8, for example, shows high resolution spectra of the peaks at 81 Da for TiO_2 nanocoated paper and the reference paper. It was observed that the peak at $m/z = 81$ is separated into peaks for TiO_2H^+ (80.95), $\text{C}_3\text{H}_5\text{O}^+$ (81.03), and C_9H_7^+ (81.07). The intensity of the positive ion peak at $m/z = 81.07$ decreased after UVA irradiation, but

Figure 5. Positive ion spectra for the reference paper before and after three different surface treatments: UVA irradiation, UVA irradiation with subsequent oven treatment, and oven treatment only for (a) $m/z = 0–100$ Da and (b) $m/z = 100–300$ Da.

increased after oven treatment. When UVA irradiation with subsequent oven treatment was applied to the reference paper, only minimal changes were observed in the peaks at 81 Da.

Figure 9 shows the distribution of the ToF-SIMS peak at $m/z = 55$ on the TiO_2 -nanocoated paper and reference paper surfaces. This peak is related to the hydrocarbon C_4H_7^+ . As expected, for the TiO_2 nanocoated paper, there is a clear decrease in the peak intensity after UVA irradiation and an increase after oven treatment, but the corresponding changes are not visible for the reference paper. These results confirmed previous observations of chemical changes that occur on TiO_2 -nanocoated paper surfaces.

Similar changes on the TiO_2 surface were observed for the peaks associated with hydrocarbon fragments containing a single oxygen. Figure 10 compares the distributions of Ti related peaks at $m/z = 48, 64$, and 81 to the distribution of peaks at $m/z = 31, 45$, and 46 , which are related to the CH_3O^+ , $\text{C}_2\text{H}_5\text{O}^+$, $\text{C}_2\text{H}_6\text{O}^+$

Figure 6. Selected hydrocarbon fragments from TiO_2 -coated paper.

Figure 7. Selected hydrocarbon fragments from reference paper.

Figure 8. High-resolution spectra of peak $m/z = 81$: reference paper on the left, and TiO_2 nanocoated paper on the right.

ion fragments on the TiO_2 nanocoated surface and on the reference sample. It can be seen that the distribution of these groups on the paper surfaces changes after UVA treatment. The signal intensity of the oxygen-containing groups increased for the TiO_2 nanocoated paper, but not for the reference paper.

4. DISCUSSION

The ToF-SIMS analysis was used to evaluate the chemical changes occurring on the TiO_2 nanoparticle-coated paper surface. The wetting properties of such paper surface can be changed from hydrophobic to hydrophilic by UVA exposure

and recovered by heat treatment from the hydrophilic to the hydrophobic state. Superhydrophobicity of a surface requires a combination of appropriate surface texture and chemistry. The surface roughness characteristics of the TiO_2 nanoparticle coated paper, as analyzed by scanning electron microscopy (SEM) and atomic force microscopy (AFM), is reported in ref 8. The surface consists of clustered 20–40 nm TiO_2 nanoparticles, characterized by the following ISO surface roughness parameters: RMS roughness $S_q = 94$ nm, surface area ratio $S_{dr} = 212\%$, and number of maxima per unit area $S_{ds} = 472/\mu\text{m}^2$.

Figure 9. ToF-SIMS images of positive mode of peak $m/z = 55$ related to $C_4H_7^+$ molecules for TiO_2 nanocoated paper (upper row), and the reference paper (lower row). Images a and e show untreated samples; images b and f show UVA irradiated samples; images c and g show samples subjected to oven treatment only; and images d and h show samples subjected to UVA irradiation with subsequent oven treatment.

To avoid the chemical complexity of a paper substrate, we also used an aluminum foil with TiO_2 nanoparticles deposited with the same parameters as for the paper samples. However, the TiO_2 nanoparticle coating on the aluminum foil resulted in a much lower water CA ($\approx 83^\circ$) than for the superhydrophobic nanocoated paper sample (CA $\approx 161^\circ$). UVA treatment of the nanocoated aluminum foil did induce superhydrophilicity (CA $\approx 6^\circ$), but subsequent oven treatment did not lead to superhydrophobicity, which was the case for the paper sample. Various substrates such as glass, ceramic, and metal surfaces have been coated with TiO_2 nanoparticles by LFS deposition^{7,12,13,42} albeit only the TiO_2 nanocoatings on paper-based substrates have shown to yield superhydrophobicity.^{8,9,24,34–37} Furthermore, TiO_2 -nanocoated paper-based substrates clearly differ from pure TiO_2 films that exhibit hydrophilic character.³¹ This means that in order to create and recover the superhydrophobicity of the paper samples within the short time scale used in our work, the role of the paper substrate is essential.

The results obtained in the current work with ToF-SIMS are in good agreement with our previous studies of the TiO_2 nanoparticle coated surface,^{9,34} in which the XPS analysis showed that after UVA irradiation, the intensity of the carbon peak

decreases, whereas the intensity of the oxygen peak increases. In contrast, after UVA irradiation and subsequent oven treatment, it was observed that the intensity of the carbon peak increases, but the intensity of the oxygen peak decreases. A more specific investigation of the sample surface, and decomposition of C 1s, O 1s, and Ti 2p peaks showed that the chemical changes occurred mainly for band regions of C 1s and O 1s peaks, whereas the Ti 2p peak was unchanged and showed the characteristic spin-orbit (1/2, 3/2) Ti^{4+} of titanium–oxygen bonds in TiO_2 . High-resolution XPS spectra showed that the C 1s peak consists of four different areas associated either to the carbon in hydrocarbon chains, or the carbon bonded to one, two, or three oxygen molecules. The oxygen peak O 1s was resolved into three peaks related to the oxygen of titanium dioxide, or to oxygen containing groups such as hydroxyl groups or carboxyl groups. On the basis of the analysis and different ratios between C, O, and Ti peaks extracted from the XPS spectra, it was concluded that chemical changes are related to the degree to which hydroxyl groups and aliphatic chains rich in carboxyl groups are either adsorbed or desorbed on the TiO_2 surface. The current work further analyzes the composition of the outermost surface layer of the

Figure 10. ToF-SIMS images of positive ion mode peaks at $m/z = 48$, 64, 81 for TiO_2 -coated paper (upper row) before and after UVA irradiation. The middle and lower rows show images in positive ion mode of peaks $m/z = 31$, 45, and 46 for the TiO_2 nanocoated paper (middle row) and the reference paper (lower row). The peaks at $m/z = 31$, 45, and 46 were related to CH_3O^+ , $\text{C}_2\text{H}_5\text{O}^+$, and $\text{C}_2\text{H}_6\text{O}^+$ ion fragments.

paperboard, which is especially important in the case of complex organic surfaces.

Many studies have been performed on the photocatalytic activation of TiO_2 under UVA irradiation,^{3–5,21,43–45} but a detailed explanation of the phenomenon is still lacking. A possible reason might be simply that the changes occur on the very outermost sample surface. In this sense, distinguishing the signals of a real sample from those of the background is challenging.

As shown by the ToF-SIMS spectra, both the TiO_2 nanocoated samples and the reference paperboard have surfaces rich in derivatives of hydrocarbon chains and oxygenated molecules, which are characteristic of contaminants and also of the coating color components of the paperboard itself. Fragments of high molecular weight additives, such as the surfactants used in kaolin or latex manufacturing and processing, cover pigment particles, resulting in additional peaks, mostly in the range of 200–700 Da.^{26,46} Kaolin used here is a hydrated aluminum silicate clay with a large number of ions contributed by additives. Thus, the spectra consist of both the peaks corresponding to these chemical fragments and the particle-related peaks. As expected, strong signals for titanium isotopes such as TiH^+ , TiO^+ , and TiO_2^+ were observed.

The UVA exposure of the TiO_2 surface in air produced clear changes in the mass spectra of the samples. The relative amounts of carbohydrates at the TiO_2 surface decreased after UVA irradiation, but there was no change in the titanium related peaks. These support the previous XPS analysis³⁴ that showed a decrease of the carbon to oxygen ratio associated to organic contaminants. Our ToF-SIMS findings agree well with those of a previous study by Gnaser,⁴⁷ which describes the

catalytic activity of TiO_2 in the decomposition of surface contaminants upon exposure to UV light. The deposited TiO_2 nanoparticles are in anatase crystalline form and photocatalytically active. Aromaa et al.⁴² have shown that the temperature and nucleation mechanism in the LFS process favor the formation of anatase.

In the present work, subsequent heat treatment of the samples in an oven resulted in a second set of changes, including the activation of chemical species that probably originate from the paper substrate such as volatile latex derivatives, e.g., a strong increase in the peak at $m/z = 91$ Da associated with C_7H_7^+ ion fragments, which were then adsorbed onto the surface. However, the origin of the hydrocarbon chains is still unknown since the oven was operated in air, which might also be a source of contaminants.

The cyclic conversion of the water CA correlates well with the ToF-SIMS results, analyzed in terms of the fragment ion species in the high-resolution spectra and the images collected from surfaces. For instance, for the TiO_2 sample, the intensity of the hydrocarbon peak C_4H_7^+ decreased after UVA irradiation, but oven treatment increased the value to a much higher level. The ToF-SIMS images showed a strong increase in the number of oxygenated molecules after UVA irradiation, which did not change after oven treatment.

The results suggest that the initially superhydrophobic TiO_2 nanoparticle-coated paper surface created by the LFS process has a distinct hydrocarbon layer rich in carboxyl-terminated groups and hydroxyl-terminated groups. This layer undergoes changes in response to UVA irradiation and oven treatment. After UVA irradiation, the TiO_2 surface is rich in activated sites such as radicals, so it becomes hydrophilic. After irradiation, when the sample is exposed to air, positively charged molecules begin to be adsorbed. This phenomenon, which has been reported in the literature,^{3–5,21,43–45} normally occurs on the thermodynamically unstable TiO_2 surface. Heat treatment induces a reverse conversion process, which is faster,²¹ so wettability conversion can occur within a short time in an oven. Because the titanium structure below the outermost layer is chemically stable,³⁴ the reversible hydrophilic to hydrophobic conversion of the TiO_2 nanoparticles lasts longer than a single cycle.

The ToF-SIMS technique can provide valuable insight into monolayer chemistry, providing an explanation of the wetting properties observed with TiO_2 nanoparticle-coated paper. We believe that the unique coating structure created by the LFS process on the paper sample by the deposition of TiO_2 surface nanoparticles is a sophisticated combined effect involving the surface chemistry and the surface structure.

5. CONCLUSIONS

Paper or paperboard substrates provide a unique superhydrophobic behavior with LFS-deposited TiO_2 nanoparticles on surface. This work developed a fundamental understanding of the chemical changes occurring on such a TiO_2 nanocoated paper surface subjected to UVA irradiation and heat treatment. An initially superhydrophobic nanocoated surface can be made hydrophilic via UVA irradiation, and then converted back into a superhydrophobic surface by heat treatment in an oven. A ToF-SIMS technique was used to show that modifications occur primarily in the chemistry of the outermost surface layer. The changes observed in the water CA are related to the chemical transformations occurring on the TiO_2 surface. It was found that UVA irradiation induces photocatalytic oxidation, and

consequently, high hydrophilicity of the TiO₂ surface. By contrast, heat treatment converts a hydrophilic surface back into a hydrophobic surface. The loss of hydrophilicity of a TiO₂ surface is related to an increase in the number of carboxyl-terminated molecules. The results, which are in good agreement with previously reported wettability and XPS measurements, are useful for engineering functional paper surfaces.

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Notes

The authors declare no competing financial interest.

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