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Hierarchical Amorphous Nanofibers for Transparent Inherently Super-Hydrophilic Coatings

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Ultra-high specific surface area, hierarchical TiO\textsubscript{2} nanofibers were synthesized by electrospinning and directly self-assembled into highly porous films for application as transparent super-hydrophilic coatings. The evolution of the coating key structural properties such as fiber morphology and composition was mapped from the as-prepared sol-gel up to a calcination temperature of 500 °C. Main fiber restructuring processes such as formation of amorphous Ti-O bonds, crystallization, polymer decomposition and the organic removal were correlated to the resulting optical and wetting performance. Conditions for low-temperature synthesis of hierarchical coatings made of amorphous, mesoporous TiO\textsubscript{2} nanofibers with very high specific surface area were determined. The wetting properties of these amorphous and crystalline TiO\textsubscript{2} nanofiber films were investigated with respect to the achievement of inherently super-hydrophilic surfaces not requiring UV-activation. The surface stability of these amorphous TiO\textsubscript{2} nanofibers was assessed against current state-of-the-art crystalline super-hydrophilic TiO\textsubscript{2} preserving excellent anti-fogging performance upon extended period of time (72 h) in darkness.

Introduction
Since their first synthetic fabrication over a decade ago, super-hydrophilic surfaces have attracted substantial scientific interest\textsuperscript{1} as they achieve a water sheeting effect within a very short timeframe (ca. 0.5 s)\textsuperscript{2-5}. The resulting implications with respect to the condensation, evaporation and transport of (non- and atmospheric) water have led to their consideration for numerous commercial applications, including anti-fogging,\textsuperscript{6,7} self-cleaning,\textsuperscript{8} anti-fouling,\textsuperscript{9} bio-implants,\textsuperscript{10} micro-lenses,\textsuperscript{11} lab-on-a-chip,\textsuperscript{12} microfluidics,\textsuperscript{13} fog-harvesting,\textsuperscript{14} and heat transfer enhancement.\textsuperscript{15}

Several lab-scale methods have been successfully established for the synthesis of super-hydrophilic coatings including plasma, electrochemical treatment,\textsuperscript{9} reactive ion etching,\textsuperscript{8} micropatterning\textsuperscript{16,17} and flame spray pyrolysis.\textsuperscript{18} However, their wetting mechanism is still intensely debated. The complete spreading of a water droplet on a surface (perfect wetting) is expected on materials having high water affinity such as that generated by high surface concentrations of hydroxyl (-OH) groups.\textsuperscript{19,20} As a result, ideal super-hydrophilicity leads to a contact angle (θ) nearing 0 and is attributed to the presence of a layer of volatile organics / gas molecules rapidly adsorbing onto the surfaces of these materials.\textsuperscript{19,20}

To overcome these limitations, morphological modifications such as surface texturing have been utilized to enhance chemically-driven water spreading over that of perfectly flat surfaces.\textsuperscript{21}

Titanium dioxide (TiO\textsubscript{2}) is a widely utilized photocatalytic and ultraviolet (UV)-augmented material with high H\textsubscript{2}O affinity that has been investigated for its photoactive,\textsuperscript{22,23} self-cleaning,\textsuperscript{24,25} optical\textsuperscript{25} and chemical sensing\textsuperscript{26} properties. Traditionally, the super-hydrophilicity of TiO\textsubscript{2} films has been found to correlate closely to UV exposure.\textsuperscript{1,27,28} For instance, UV-induced super-hydrophilicity has been investigated using thin sol-gel-made polycrystalline TiO\textsubscript{2} films annealed at 500 °C. These films required surface activation, becoming super-hydrophilic when exposed to UV irradiation and hydrophobic when kept in the dark.\textsuperscript{1} Similar behaviors have been observed for amorphous TiO\textsubscript{2} films.\textsuperscript{27,28} This is a main limitation of TiO\textsubscript{2} that is known to lose super-hydrophilicity within a few minutes\textsuperscript{29} to one day\textsuperscript{19,29,30} upon last exposure to UV-light.

Doping of sol-gel-made TiO\textsubscript{2}\textsuperscript{31,29} and mesoporous surface enhancement\textsuperscript{31} have been used to promote UV-independent super-hydrophilicity. Highly rough TiO\textsubscript{2} films deposited by metal-organic vapor deposition were found to prevent the oxidation of Ti\textsuperscript{3+} during periods of darkness and were able to maintain super-hydrophilicity for extended periods (2-3 days) post UV-activation.\textsuperscript{31} Amongst other TiO\textsubscript{2} synthesis methods, electrospinning is a scalable, atmospheric process that offers several structural advantages. Electrospin coatings are
continuously self-assembled during fiber synthesis, leading to a very porous multi-layer structure having considerably higher flexibility than PVD/CVD-made films and mechanical stability than aerosol-deposited nanoparticle layers. Electrospinning of polyvinyl pyrrolidone-Titanium (IV) Isopropoxide (PVP-TTIP) sol-gel mixtures has led to some of the thinnest TiO$_2$ fibers so far reported. However, the optimization of electrospun TiO$_2$ nanofiber composition and morphology for fabrication of UV-independent, super-hydrophilic coatings has not yet been reported.

Here, the synthesis of amorphous TiO$_2$ nanofibers for the fabrication of transparent and inherently super-hydrophilic coatings has been investigated. The evolution of the key fiber structural properties was mapped as a function of calcination temperature in terms of morphology, bulk and surface compositions leading to a well-characterized set of amorphous and crystalline TiO$_2$ nanofiber coatings. Structural-functional correlations of these materials have been established with respect to their wetting and optical properties. A novel hierarchical amorphous TiO$_2$ nanofiber morphology with excellent anti-fogging performance was identified and compared to state-of-the-art anatase crystalline coatings.

**Experimental**

**Materials and Fabrication**

Nanofibers were obtained by electrospinning of an ethanol-based sol-gel (0.06 g/mL PVP and 0.0936 g/mL Ti(OiPr)$_4$), with acetic acid as a hydrolysis promoter. A PVP solution was first prepared by dissolving 0.6 g of PVP (Sigma Aldrich, Mw = 1,300,000) in 5 mL of ethanol (Sigma Aldrich, 200 proof). A sol-gel solution was then prepared using 2 mL of ethanol, 2 mL of acetic acid (glacial, Chem-Supply) and 1 mL of Ti(OiPr)$_4$ (Sigma Aldrich). Solutions were stirred for 10 minutes before introducing the sol-gel mixture into the PVP solution. A clear yellowish solution was obtained, which was electrospun after 1 hour of mixing. An applied voltage of 25 kV was used with a working distance and flow rate of 20 cm and 0.8 mL/hour, respectively, providing homogenous coverage of nanofibers on the glass substrates. Surface coverage was confirmed by optical microscopy. A deposition time of 1 minute was used to obtain clear, transparent coatings. Once collected on glass slides, the coatings were stored at room temperature for 5-6 hours to allow for the completion of hydrolysis. Samples were then calcined for 1 hour (3 °C/min) between 100 °C and 500 °C ($T_1$).

**Characterization**

Calcined coatings were then kept in the dark at room temperature for 3 days before proceeding to the wetting studies. The dynamic water contact angle (CA) was measured by placing a drop of deionized water (5-6 µL) on the sample surface using a KSV CAM200 contact angle goniometer (Finland) with a heliopan ES43 camera (Japan). The CA was computed by a commercially available (CAM2008) program. Samples were analyzed using a Zeiss UltraPlus analytical scanning electron microscope (FESEM) at 3kV and a Hitachi H7100FA 125kV transmission electron microscope (TEM). Prior to examination, SEM specimens were platinum sputter-coated for 2 min at 20 mA. Average fiber diameters ($d_{avg}$) were determined by counting with ImageJ 20 fibers in each SEM image. TEM specimens were suspended and dispersed in ethanol (Sigma Aldrich, 200 proof) before they were deposited on 200-mesh nickel-copper grids (Formvar) and dried at room temperature. UV-vis analysis was conducted using a microplate reader (Tecan 200 PRO, Switzerland) from 300-800 nm with 10 scans per cycle. The crystal phases, size ($d_{XRD}$) and surface compositions were analyzed by X-Ray diffraction (XRD, D2 Phaser, Bruker, U.S.A) and Fourier transform infrared spectroscopy (FTIR-ATR, Bruker-Alpha, U.S.A). Amorphous samples in XRD (< 400 °C) were normalized using the first crystalline anatase 101 peak achieved at 400 °C. The Brunauer-Emmett-Teller specific surface area (BET, SSA), pore volume and distribution of the as-prepared coatings were measured by $N_2$ adsorption using a porosity analyzer (Micromeritics, TriStar II, U.S.A). All samples were degassed at 300 °C for 5 hours prior to analysis. Evaluation of the antifogging performance was conducted on selected coatings, on calcined coatings (300 °C, 350 °C and 500 °C) by exposure to a vapor stream 40 cm above boiling water for 5 - 10 s, as previously reported. Thermogravimetric (TGA) and differential thermogravimetry (DTG) analysis were conducted from 100 - 800 °C (3 °C/min ramp) and isothermally at 350 °C for 1hr under atmospheric conditions (Perkin Elmer, STA 8000, U.S.A).

**Results and Discussion**

**Synthesis and Characterization of Hierarchical Nanofibers**

The as-prepared nanofibers had a flexible structure with notable formation of hoop and spiral shapes (Figure 1a) upon evaporation of the solvent utilized for TEM preparation. Their appearance was flaky, revealing a porous morphology and a very rough surface. Upon low temperature ($T_1 = 250-350$ °C) calcination, the fibers’ diameters shrunk rapidly (Figures 1b and 1c) leading to increased rigidity and relatively smooth surface morphologies. Increasing the calcination temperature to 500 °C had minimal impact on the fiber size but increased surface roughness, resulting in a granular appearance with a grain size of ca. 20 nm (Figure 1d, inset). This is in line with previous reports on high-temperature calcined TiO$_2$ fibers, attributing this morphology to crystal nucleation.

![Fig. 1 TEM images of (a) as-prepared and calcined at (b) 250 °C, (c) 350 °C and (d) 500 °C TiO$_2$ nanofibers.](image-url)
The SEM analysis (Figure 2) of the coatings supported these observations with the average fiber count diameter decreasing from 412 nm ±104 nm of the as-prepared (Figure 2a) to 80.8 nm ±44.5 nm of the 500 °C calcined samples (Figure 2f). The largest reduction in fiber diameters from 210 to 128 nm was observed with increasing temperature from 300 to 500 °C. Detailed analysis from 350 to 500 °C revealed that roughening and restructuring of the fiber surface occurs for T ≥ 400 °C. This was in-line with the granular morphology observed by TEM (Figure 1d, inset) and is attributed to the nucleation of TiO$_2$ crystals on the nanofiber surfaces (Figure 2d).

Although the visible TEM and SEM fiber diameter decreased monotonously with increasing calcination temperature, the available surface for water adsorption was maximal below 500 °C. Figure 4 shows the specific surface area (SSA) of the fibers (Figure 4, triangles) as a function of the calcination temperature. The SSA increased drastically from ca. 65 to 106 m$^2$/g with increasing T$_s$ from 300 to 350 °C. This is only partially justified by the fiber diameter reduction observed by SEM and TEM (Figure 2b,c) and is mainly attributed to the formation of a mesoporous surface structure. The decrease in fiber diameters is attributed to the desorption of (PVP) polymer residuals.

The XRD spectra of the calcined samples (Figure 3) provided further understanding of the observed surface restructuring (Figure 1 and 2). Up to a calcination temperature of 350 °C, the TiO$_2$ nanofibers were amorphous with no visible diffraction peaks (Figure 3). At T$_s$ of 400 °C, anatase crystals with an average size of 8.8 nm were nucleated. Further increasing T$_s$ (450 °C) increased the crystal size to 12.0 nm preserving the pure anatase structure. At 500 °C, the formation of a small amount (8.2 wt%) of rutile was observed and the anatase d$_{XRD}$ reached 17.4 nm. This is in line with the TEM morphology observed at 500 °C and suggests that the multi-granular texture of the fibers is due to the formation of large anatase crystals.

Increasing the calcination temperature step-wise to 500 °C resulted in a 50% SSA reduction. This was characterized by an initial SSA drop to 42±5 m$^2$/g at 450 °C and thereafter its leveling-off up to 500 °C. Considering that the fiber diameter of the 350 °C calcined samples was slightly larger than that of the 500 °C ones, the higher SSA of amorphous TiO$_2$ nanofibers indicates a mesoporous surface morphology. This is further supported by the large pore volume and small (4.7 nm) average pore size measured upon partial removal of the organic scaffold at 350 °C (Table 1).

At a higher magnification (Figure 1c, inset) the smooth-appearing fibers calcined at 350 °C had a more discrete structure, suggesting the presence of nano-scale pores. The high SSA achieved here by these amorphous nanostructures (T$_s$ = 350 °C) is comparable to the highest reported for TiO$_2$ nanofibers$^{26,37,38}$ and is, to the best of our knowledge, also the highest ever achieved with the PVP-TTIP system. The hierarchical morphology of these amorphous fiber coatings combines the macro-scale porosity of the fiber layers (Figure 2c) with the nano-scale roughness of their mesoporous surface (Figure 4a,b) offering an optimal structure for the rapid penetration and spreading of water.

**Table 1** Properties and performance of the TiO$_2$ fibers, and comparison with selected literature data.

<table>
<thead>
<tr>
<th>Morphology</th>
<th>d$_{EM}$ nm</th>
<th>SSA m$^2$/g</th>
<th>PV cm$^3$/g</th>
<th>CA$_i$ °</th>
<th>CA$_d$ °</th>
<th>Ref.</th>
</tr>
</thead>
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<tr>
<td>Amorphous TiO$_2$ fibers</td>
<td>128</td>
<td>105.8</td>
<td>0.100</td>
<td>8.5</td>
<td>9.2</td>
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<td>T$_s$ = 350 °C</td>
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<td>92 wt% anatase fibers</td>
<td>81</td>
<td>44.8</td>
<td>0.076</td>
<td>0.0</td>
<td>7.0</td>
<td>This work</td>
</tr>
<tr>
<td>T$_s$ = 500 °C</td>
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</tr>
<tr>
<td>ES anatase fibers</td>
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<td>60</td>
<td>-</td>
<td>2.0</td>
<td>-</td>
<td>23</td>
</tr>
<tr>
<td>ED Amorphous NPs</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>12</td>
<td>39</td>
<td>27</td>
</tr>
<tr>
<td>FSP NPs</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>5-8</td>
<td>10</td>
<td>15</td>
</tr>
</tbody>
</table>

d$_{EM}$ – fiber diameter determined by electron microscopy. PV – pore volume of fibers. CA$_i$ – initial contact angle upon synthesis. CA$_d$ – contact angle after incubation in darkness for > 12 hours. ED – Electrodeposited. FSP – Flame spray pyrolysis. ES – Electrospin. NPs – Nanoparticles.

**Optical and Wetting Performance**

The optical performance of the nanofiber coatings was investigated as a function of the calcination temperature. Figure...
5 shows the transmittance at an incoming light wavelength of 400 nm (circles) and 600 nm (triangles) from the as-prepared to the 500 °C calcined samples. The as-prepared coatings' transmittance was ca. 77.5% for both wavelengths. This was attributed to the presence of PVP and large fiber diameters (ca. 440 nm), leading to strong light scattering and absorption. Calcining the samples to 250 °C increased transmittance by ca. 10%, in line with the suggested partial decomposition and desorption of the PVP matrix.

Increasing $T_s$ to 350 °C gradually increased the transmittance up to ca. 92.5% and thus ca. 2.5% below that of the bare glass slides. Further increments in $T_s$ (up to 500 °C) did not enhance light transmittance. This is in line with the stabilization of the fiber diameter observed by SEM and TEM (Figure 1 and 2) and the relatively small amount of organic residuals detected by FTIR at 350 °C (Figure 8). Transmittance values between 85% to 90% are considered sufficient for most optical applications. The coating performance obtained here is comparable to state-of-the-art coatings, showcasing the suitability of these amorphous nanofibers for applications in micro-lenses, solar cells and photo-detectors.

The long-term coating wetting properties were quantified as a function of the calcination temperature by measurement of the dynamic contact angle with a water droplet upon keeping the samples in the dark for 72 h ($\theta_d$). Figure 6 compares the dynamic water contact angle for the 350 °C (triangles) and 500 °C (square) calcined coatings with bare glass (circles).

Upon a contact time of 0.5 s, the $\theta_d$ of the bare glass converged toward ca. 25°. In contrast, the glass with the 350 °C and 500 °C coatings reached a $\theta_d$ of ca. 8.1±1° ($t_c = 0.5$ s). Although the latter had a slightly lower $\theta_d$ (Table 1), these effects were minimal, and the actual performance was almost indistinguishable with both coatings satisfying super-hydrophilic requirements. This is attributed to the larger SSA and pore volume of the amorphous fibers (Table 1) compensating for the higher H$_2$O affinity of the anatase surface. It is worth noticing that the initial contact angle at 0.5 s ($\theta_d$) of the 500 °C samples (Table 1) was 0° indicating a partial deactivation of the anatase surface upon 72h in darkness. In contrast, for the amorphous fibers the initial (8.5°) and post-light deprivation (9.2°) contact angles (Table 1) were nearly identical suggesting inherent super-hydrophilicity.

Figure 7 shows the initial dynamic water contact angle at 0.5 s as a function of the calcination temperature. The as-prepared coatings (Figure 7) were hydrophobic with a CA of 115°. The $\theta_d$ decreased sharply with increasing calcination temperature with an asymptotic behavior. The largest CA drop occurred from 100 to 250 °C ($\theta_d_{250°C} = 25°$). Further increasing $T_s$ to 350 °C led to a $\theta_d$ of below 10° and thus to
the attainment of super-hydrophilicity (CA$_{d,350°C}$ = 9.2$^\circ$). Small reductions ($\approx 1^\circ$) in CA were obtained for $T_c \geq 400$ °C. To assess the durability of the films, subsequent multi-drop tests were conducted on the 350 °C and 500 °C calcined films. No variation of the water contact angle and macroscopic film structure was observed up to 6 hours wetting-drying cycles.

The coating anti-fogging performance was assessed by placing the bare and coated glass slides in a water vapor stream. Uncoated glass fogged within a few seconds due to the condensation of water droplets (Figure 7, insets). The coating calcined at 300 °C demonstrated reduced fogging and improved transmittance. However, the background visibility was still severely hindered by partial fogging. The coatings calcined at $T_c \geq 350$ °C demonstrated excellent anti-fogging performance with a clear and transparent appearance during the entire period of vapor exposure. This indicates that both a mesoporous surface and removal of most organics are required to obtain super-hydrophilicity. These results show, for the first time, that low-temperature synthesized amorphous TiO$_2$, not requiring UV-activation, can achieve comparable wetting performance as crystalline anatase assembled at high-temperatures.

**Nanofiber Surface Analysis**

To explain the strong variation in wetting and anti-fogging performance observed from 300 to 350 °C, the fiber surface composition was investigated by FTIR. The onset of PVP scaffold decomposition was found to take place between 250-350 °C, in line with previous reports$^{[9,40]}$ where diminishing organic peaks$^{[4]}$ such as C=O stretch at 1650 cm$^{-1}$, CH$_2$ twist, wag and C-N stretch at 1200-1300 cm$^{-1}$ occurred. The Ti-O bonds were found to become predominant at a calcination temperature of 250 °C as indicated by strong inorganic Ti-O peaks$^{[42]}$ between 450-550 cm$^{-1}$. This explains the strong drop in contact angle ($\Delta$CA = 90$^\circ$) observed for calcination temperatures above 200 °C (Figure 7).

Further increasing the calcination temperature led to a reduction of organic related peaks that completely disappeared only at 400 °C. These findings further indicate that the fiber diameter and shrinkage dynamics is controlled by the decomposition and desorption of the polymer precursor (Figures 1 and 2). The remaining organic peaks (~1650 cm$^{-1}$) at 350 °C were mostly attributed to distorted C=O, and appeared to have a minimal impact on the surface water affinity (Figure 7). A peak at 2340 cm$^{-1}$ was also found for $T_s \geq 400$ °C, suggesting the presence of physisorbed carbon dioxide (CO$_2$). This is in line with previous reports indicating considerable adsorption of atmospheric CO$_2$ on crystalline TiO$_2$. It is worth noting that, even after an extended incubation period of 8 days, the amorphous TiO$_2$ ($T_s = 350$ °C) did not develop this CO$_2$ peak (not shown). This is in line with the TGA analysis of the fiber mats (Figure S1) showing that most of the organics are desorbed between 300 and 400 °C. Furthermore, analysis of the organics desorption dynamics at isothermal conditions (Figure S2) suggests that the critical transitional temperature for organics removal and achievement of super-hydrophilicity is close to 350 °C.

**Conclusions**

An optimal TiO$_2$ nanofiber morphology was determined for fabrication of flexible, non-UV augmented super-hydrophilic coatings having superior transparency and anti-fogging performance. For the first time, it is shown that very-high SSA (> 100 m$^2$/g), hierarchical, amorphous TiO$_2$ nanofibers, not requiring UV activation, have comparable inherent wetting performance to crystalline anatase. These amorphous fiber coatings were synthesized by rapid (1 min) electrospinning leading to enhanced and prolonged (72 h in the darkness) super-hydrophilicity. It was found that amorphous Ti-O bonds

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Fig. 7 Dynamic water contact angle and (insets) optical images of water droplets as a function of the calcination temperature. Optical images (top right insets) of bare and coated glass in a water vapor stream.

**Fig. 8 FTIR spectra** (a) of electrospun TiO$_2$ nanofibers as a function of the calcination temperature ($T_c$). Magnifications of the FTIR spectra from (b) from 2300 cm$^{-1}$ to 2400 cm$^{-1}$ depicting atmospheric CO$_2$ adsorption, and (c) from 1100 cm$^{-1}$ to 1900 cm$^{-1}$ depicting the loss of organics between 250-400°C.
become predominant at 250 °C leading to a considerable reduction (ACA = 90°) of the water contact angle. Calcination at 350 °C was required to remove most residual organics and obtain quasi-perfect wetting (CA at 0.5 s < 10°). These low-temperature synthesized amorphous nanofibers have potential for development of super-hydrophilic coatings with numerous applications such as anti-fog glass, microfluidic devices and water filtration membranes.

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Notes and references

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