

## Research Article

# A Study of Factors that Change the Wettability of Titania Films

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The effect of several pretreatment methods on the wettability of polycrystalline titania-coated glass (Pilkington Activ) and plain glass are investigated. UV/ozone, immersion in aqua regia, and heating ( $T > 500^\circ\text{C}$ ) render both substrates superhydrophilic (i.e., water contact angle (CA)  $< 5^\circ$ ). The dark recovery of the contact angles of these superhydrophilic substrates, monitored after treatment in either an evacuated or an ambient atmosphere, led to marked increases in CA. Ultrasound treatment of superhydrophilic Activ and glass samples produced only small increases in CA for both substrates, but rubbing the samples with a cloth produced much larger increases. The results of this study are discussed in the context of the current debate over the mechanism of the photo-induced superhydrophilic effect.

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## 1. INTRODUCTION

Titanium dioxide films have been widely observed to become superhydrophilic, that is, water droplet contact angle  $< 5^\circ$ , when exposed to ultraviolet (UV) light, a phenomenon termed photoinduced superhydrophilicity (PSH) [1–7]. Its effects have been pivotal in the development of self-cleaning surfaces for glazing and other applications, but the precise mechanism by which this change is effected remains the subject of some debate, although it is clear that PSH is initiated by the photogeneration of electron/hole pairs and their migration to the surface. An essential feature of the overall PSH phenomenon is not only the initial, photo-induced hydrophobic to hydrophilic change, but also the reverse, dark process, whereby a superhydrophilic titania film recovers its original hydrophobic form. Any mechanism of PSH must embrace both the light-induced superhydrophilic process and the dark hydrophobic recovery step.

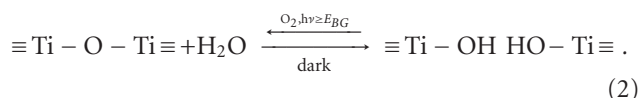
In 1985 Kume and Nozu of Nihon Itagarasu, Japan reported that sheet glass coated with  $\text{TiO}_2$  had the ability to stay clean by "...rapidly and automatically decomposing and removing organic stains adhered to the glass surface..." [8]. Most importantly, part of their patent application involved the observation that the contact angle made by a water

droplet on the glass, that is, CA, was reduced as a function of UV irradiation time. This appears to be the first clear claim of a PSH effect relating to titania films on glass and explanation for the effect, namely, it is due to the removal of hydrophobic organic stains on the surface, via the following, well-established, photocatalytic oxidative (PCO) process:



In contrast, in 1997, Wang et al. [6], reporting on the UV-induced PSH of  $\text{TiO}_2/\text{SiO}_2$  films, proposed that the effect was not due to PCO but rather the dissociative adsorption of water at surface defects created by UV light [9]. The defects, it was suggested, were formed by the trapping of holes at bridging oxygen lattice points close to the surface, the  $\text{Ti}^{4+}$  sites being reduced to  $\text{Ti}^{3+}$  by the electrons and oxygen atoms being ejected to form vacancies [10]. The oxygen vacancies were thought to cause an increase in the adsorbed hydroxyl group density and lead to the formation of hydrophilic regions. It was proposed that storage in the dark, in the presence of oxygen, removed the defects replacing the chemisorbed hydroxyl groups with oxygen and so returning the surface to its original hydrophobic state. A very simple summary of this surface reorganisation

mechanism for PSH is as follows:



It has been suggested that the above mechanism is specific to only a few materials of which titania is most notable, for example, it is not exhibited by silica substrates, that is, glass. This photo-induced surface reorganisation (PISR) model of PSH has received support from a number of different studies including examination of the creation of  $\text{Ti}^{3+}$  defects on single-crystal rutile  $\text{TiO}_2$  using XPS [11]; FTIR measurements that reveal anatase  $\text{TiO}_2$  is able to adsorb water reversibly upon UV irradiation [10]; and AFM studies which show apparent “roughening” of the surface as a result of UV exposure (attributed to defect formation) [12]. The importance of bridging oxygen, an integral part of the PISR model, has also been illustrated using rutile single crystals, with the (001) face—which does not feature bridging oxygens—showing the least propensity to photo-induced hydrophilic change [10, 13].

Recently, support for the more simplistic PCO model of PSH, based on reaction (1), namely, the photocatalytic removal of hydrophobic organic surface contaminants, has increased with a number of different groups reporting evidence for this model using test hydrophobic surface contaminants such as trimethyl acetate [14] and hexane [15], and the detection of previously unobserved layers of hydrocarbons on titania surfaces [16]. These results have presented a significant challenge to the PISR model of PSH.

Key to any model of PSH is an explanation of the dark recovery step, and significant support for this aspect of the PISR model of PSH effectively a dark, dehydration step (see reaction (2)) has been provided by studies [10, 17, 18] which show that titania films regain their original hydrophobicity at an increased rate when stored at increased temperatures [18, 19] or under an evacuated ( $\text{H}_2\text{O}$  free) atmosphere [17]. The PISR model rationale behind this is that heat and vacuum cause the metastable water/hydroxyl groups, responsible for the superhydrophilic surface of titania, to dissociate more quickly. It has also been demonstrated that hydrophilic  $\text{TiO}_2$ -glass films exhibit a measurable increase in contact angle when subjected to ultrasound [20]. The use of ultrasound to render a superhydrophilic film slightly more hydrophobic was interpreted initially by advocates of the PISR model as being due to the reoxidation of the surface by sonically produced OH radicals [20], but more recently as simply the breaking down of the photo-induced hydrophilic metastable state by an external stimulus [18]. A similar interpretation has been used to explain the effect of wet rubbing [21], which reconverts superhydrophilic titania to its original hydrophobic state via a mechanochemical effect.

In this paper, the effects of UV/ $\text{O}_3$ , heating, and strong acid pretreatment on initially hydrophobic samples of Activ and plain glass were studied. In addition, the effects of vacuum, ultrasound, and rubbing on the wettability of clean, superhydrophilic samples of titania-coated, self-cleaning glass (Activ), and plain glass were examined and the results

discussed in terms of the two different mechanisms of the PSH effect.

## 2. EXPERIMENTAL

All reagents, unless otherwise stated, were supplied by Aldrich and used as received. The titania-coated substrates used in this work were 2 cm × 2 cm Activ samples, supplied by Pilkington Glass, comprising 4 mm thick float glass coated with an approximately 15 nm layer of  $\text{TiO}_2$ , deposited by an inline CVD process [22]. The reverse side of Activ provided the samples of uncoated float-glass used in all “plain glass” blank experiments. Additional experiments revealed no difference in behaviour between that of the reverse side of Activ and uncoated float glass samples. Typically, all glass samples, that is, Activ or plain, were cleaned with chloroform and left in a sealed box in the dark for in excess of one month before use. Unless otherwise stated, both types of glass were rendered superhydrophilic by pretreating with UVC/ozone, effected by irradiation with 2 × 6 W UVC (254 nm) bulbs (Vilber-Lourmat, Torcy, France), irradiance  $\sim 1 \text{ mW cm}^{-2}$ , in a water saturated, that is, 100% relative humidity (RH), oxygen atmosphere containing  $\sim 1700$  ppm ozone, produced by a corona-discharge ozone generator (OZ500, Dryden Aqua, Edinburgh, UK).

Other pretreatment methods used included a heat-treatment process, using a muffle furnace, in which the samples were kept at the desired temperature for 1 hour before removing to cool to room temperature in a covered Petri dish. Aqua regia was also used as a pretreatment method and involved immersing the samples for 1 hour in the aqua regia before being removed, rinsed with doubly-distilled, deionised water and dried in a stream of cylinder air.

Water droplet contact angles, CAs, were measured using an FTA100 system comprising a CCTV camera interfaced with a computer, which provided a continuous stream of images of any water droplet after its initial deposition onto the surface of the substrate under test. Droplets were deposited using a 500  $\mu\text{L}$  Gastight (Hamilton) syringe, via a 30-gauge stainless steel needle with 0° bevel (Kahnetics), which deposited reproducible 5  $\mu\text{L}$  water droplets. The software package associated with the instrument allowed calculation of the contact angle made by the water droplet deposited on the substrate by curve fitting the droplet image outline. Three droplets were deposited per sample and the average of the contact angles determined with a typical variance of <5%.

The study of the kinetics of contact angle recovery of samples held under vacuum was carried out using a vacuum desiccator connected to a vacuum line. Noncovered samples were simply left on the benchtop in a light-free laboratory. For the investigation of ultrasonic (US) recovery, samples of superhydrophilic Activ or glass were immersed in doubly-distilled, deionised water and placed in a US bath (VWR model: USC100T). All glassware for this section was thoroughly cleaned with chloroform and rinsed with water before use. Sample handling was carried out using plastic

TABLE 1: Table of water contact angles for Activ and glass samples before and after pretreatment.

Pretreatment method	Activ		Glass	
	initial CA/°	final CA/°	initial CA/°	final CA/°
UVC/O <sub>3</sub> <sup>(a)</sup>	71	<5	35	<5
$\Delta$ 500°C <sup>(b)</sup>	70	<5	37	<5
Aqua regia <sup>(c)</sup>	70	<5	38	<5

<sup>(a)</sup>Samples irradiated by 2 × 6 W UVC bulbs in ~1700 ppm O<sub>3</sub> for 1 hour.

<sup>(b)</sup>Samples heated to 500°C and held at temp for 1 hour before cooling under Petri dish.

<sup>(c)</sup>Immersion in 25 mL aqua regia for 1 hour before rinsing and drying.

forceps and the samples were dried with compressed air from a cylinder.

### 3. RESULTS AND DISCUSSION

#### 3.1. Pretreatment cleaning methods

The combination of short wavelength ultraviolet light and ozone to create electronically excited ozone, O<sub>3</sub><sup>\*</sup>, a very effective oxidising agent, is well documented in its use for destroying organic materials and scouring the latter from surfaces such as semiconductor wafers [23, 24]. Recent work by this group has found that the combination of UVC and ozone as a pretreatment produces a superhydrophilic surface on Activand plain glass. These findings imply that the intrinsic state of a titania film or pristine glass is superhydrophilic, as indicated by other work on both plain glass [25] and titania [26]—such as found on Activ—and that this state requires simply the removal of all surface contaminants, particularly hydrophobic organics for its production.

The finding that UV/O<sub>3</sub> pretreatment renders Activ superhydrophilic fits in with both the PSIR and PCO models of PSH. However, the observation that plain glass is also rendered superhydrophilic indicates that the initial hydrophobic nature of the plain glass, and most probably Activ, is due to contamination of the surface by hydrophobic organics, at a level too low to be detected by simple FTIR. Thus, there appears no need to invoke a surface reorganisation mechanism, that is, PISR to explain PSH in titania, since the above results imply any oxidative process that removes hydrophobic surface organics, such as UVC/O<sub>3</sub>, will render the surface of titania and glass superhydrophilic. The typical water droplet contact angles of plain and Activ glass samples before and after UV/O<sub>3</sub> treatment are given in Table 1.

A series of experiments were carried out to investigate a variety of other oxidising pretreatment methods, including heating and strong acid immersion, to ascertain if all were able to render Activ and plain glass superhydrophilic (i.e., CA < 5°). Thus, heating Activ and plain glass at different temperatures and testing their hydrophilic natures, via CA measurements, produced the results illustrated in Figure 1. These results show that for both substrates, the CA decreases with increasing temperature, with glass falling from an initial

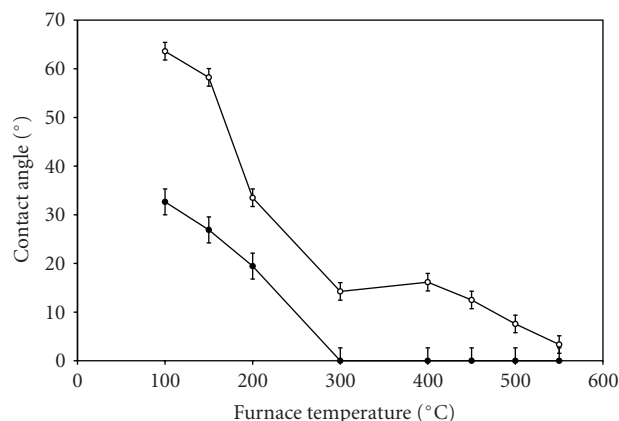


FIGURE 1: Plot of contact angle versus pretreatment temperature for Activ (○) and for glass (●).

contact angle, CA<sub>i</sub>, ~35° to <5° by 300°, and Activ from CA<sub>i</sub> ~70° to <5° by 550°.

That the titania substrates become hydrophilic with heat treatment appears at odds with the PSIR model of PSH, that is, reaction (2), which suggests that the dark dehydration process should be promoted by high temperatures [27], leading to either no change, or an increase in its hydrophobic nature and *not*, as observed in Figure 1, a decrease. Instead, the results in Figure 1 indicate that the initial hydrophobic character of Activ and plain glass is due to organic surface contaminants that are readily oxidised by high-heat treatment to reveal the intrinsic superhydrophilic nature of glass and titania films. From the data in Figure 1, it appears that the plain glass samples become hydrophilic at lower temperatures than Activ, probably due to a lower level of contamination on glass, which is much smoother than the titania films, rendering the latter more susceptible to organic adsorption.

In a final set of experiments, Activ and plain glass samples that were initially hydrophobic were pretreated with the very oxidising reagent, aqua regia, and all found to be rendered superhydrophilic (see Table 1).

From the above results, it appears that all three methods of pretreatment, that is, UVC/O<sub>3</sub>, heat (>550°C), and aqua regia are able to effect the conversion of both Activ and plain glass samples from an initial hydrophobic state to a superhydrophilic state. All three methods use very strong oxidising agents/conditions to render plain and Activ glass samples superhydrophilic, most probably due to the oxidation of any surface hydrophobic organic species. These results provide significant support for the PCO model of PSH and reveal that the pristine, that is, organic-free, surfaces of these materials are superhydrophilic.

#### 3.2. Studies of the “dark” hydrophilic to hydrophobic process

The “dark” recovery of contact angle, that is, the regeneration of hydrophobicity, exhibited by superhydrophilic titania films has been widely reported [10, 17, 22, 28], and opinion

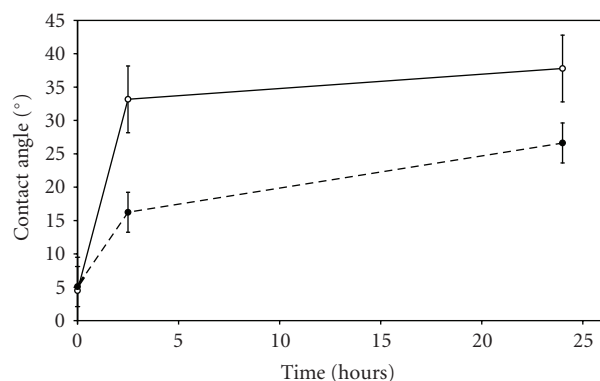


FIGURE 2: Water droplet contact (CA) angle versus exposure time in an evacuated atmosphere for Activ (○) and glass (●); CA measurements recorded under ambient conditions.

over its cause is polarised between a recontamination of the surface by airborne organics (the PCO model of PSH) and the reverse of reaction (2), that is, a dehydroxylation/dehydration process on the surface of the titania (the PISR model of PSH). Work carried out by others [17] shows that superhydrophilic samples of titania become more hydrophobic when stored in an evacuated atmosphere. These results are interpreted as providing strong evidence of the PISR model, in which vacuum storage accelerates water desorption and therefore CA recovery in superhydrophilic samples of titania. In replicating this work, we also found that the CA of Activ increases markedly when the samples are stored under vacuum, but also, and more revealing, that plain glass exhibits the same feature, although to a lesser extent. These results, illustrated in Figure 2, indicate that the phenomenon of the CA increasing for superhydrophilic titania films held under vacuum—used to support the “surface reorganisation” model, that is, reaction (2)—is not specific to titania films but is also exhibited by plain glass and so not likely to be associated with a PISR mechanism, which is attributed to titania but not to glass. Instead, the more likely explanation is that it is due to organic contamination of a clean surface, that is, glass or titania in this work, produced by exposing the sample to air when making the CA measurement after storage in a vacuum.

The effect of airborne contamination of a pristine, superhydrophilic glass, and Activ surface was demonstrated by leaving two freshly prepared samples out on the bench and monitoring the change in CA as a function of time. The results of this work are illustrated in Figure 3, from which it is clear that, on the open bench, a pristine, superhydrophilic sample of glass, or Activ can be rendered noticeably hydrophobic within few hours of exposure. Note that, as expected from its lower surface roughness, over the same time plain glass is rendered less hydrophobic than Activ due to this surface contamination. Simple IR analysis of these glass samples revealed no indication of contamination of their surfaces by hydrophobic organics, implying that the level is very low and below that detectable by conventional FTIR spectroscopy.

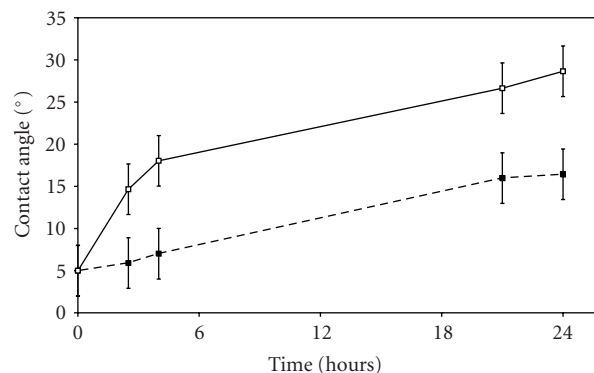


FIGURE 3: Variation in CA versus time for initially pristine superhydrophilic sample of Activ (□) and glass (■) under ambient laboratory conditions.

TABLE 2: Table of water contact angle for Activ and glass samples before and after either sonication or immersion for 10 minutes in deionised (DI) water.

Treatment	Activ		Glass	
	initial CA/°	final CA/°	initial CA/°	final CA/°
Sonication for 10 minutes in DI water	<5	8.9	3.8	8.2
DI water immersion for 10 minutes	<5	6.4	4.3	5.3

Previous work carried out by others [20] has shown that a superhydrophilic titania film is rendered more hydrophobic upon exposure to ultrasound (10 minutes). In another set of experiments, both glass and titania films, rendered superhydrophilic by treatment with UVC/O<sub>3</sub>, were placed in high-purity water in clean beakers and treated with ultrasound. The measured CAs of these samples before and after exposure to ultrasound are given in Table 2 and show that for both samples upon sonication the CA rises slightly, by 3–5°, whereas without sonication the CA remains largely unchanged. These results imply that the effect of ultrasound on superhydrophilic films, be they glass or titania, is very small and most probably due to a roughening of the substrate, and/or some organic contamination. This effect is, once again, not specific to titania and would have been expected if the PISR model was appropriate.

Other work shows that any wiping or rubbing of a pristine superhydrophilic glass or titania film using a tissue or cloth renders the film hydrophobic, and this is attributed, once again, to organic contamination of the surfaces of these substrates. It appears unlikely that rubbing is able to effect the reverse of reaction (2) via a mechanochemical effect as claimed by others [21] since plain glass is affected in the same way as titania.

#### 4. CONCLUSIONS

UV light is well known to render titania samples superhydrophilic, but this can also be effected for glass and titania



films by the combination of UVC and ozone or pretreatment with a highly oxidising solution (e.g., aqua regia) or by heating at  $T > 500^{\circ}\text{C}$ , suggesting that a common process is responsible for the cleaning of both substrates, namely, the removal of adventitious hydrophobic organic surface species via oxidation. These findings indicate that the pristine surfaces of plain glass and titania are intrinsically superhydrophilic and imply that the photocatalytic oxidation of organics on titania (PCO) is the most likely cause of the PSH effect.

Investigations of the recovery of the initial hydrophobicity exhibited by untreated titania or plain glass showed that, once rendered superhydrophilic, the dark hydrophilic to hydrophobic process is exhibited by both titania and plain glass films and is most likely due to contamination by airborne, hydrophobic organics. Thus, storage of titania or plain glass under vacuum, or on the open bench, leads to a noticeable increase in CA. The effect of ultrasonic treatment on contact angle recovery is very small for both plain and titania-coated glass, and probably due to surface roughening. Rubbing or wiping the hydrophilic plain glass or titania films produces a marked rise in hydrophobicity and is attributed to contamination of the surfaces by hydrophobic organics.

The work presented here provides further support for the proposal that the PSH effect is due to the UV-driven removal of hydrophobic surface organics by PCO, and the dark, slow readsorption of airborne organics.

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