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Marcin JANCZAREK*, Jan HUPKA*, Horst KISCH**

# HYDROPHILICITY OF $TiO_2$ EXPOSED TO UV AND VIS RADIATION

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Thin titania films can be used especially as a component of self-cleaning glass, utilizing photoinduced hydrophilic properties of titanium dioxide surfaces. For the first time thin titania layer on the Pilkington Glass Activ$^{TM}$ was modified with ammonia, thiourea and urea to introduce non-metal elements into titania structure to shift absorption spectrum to visible light region. Contact angles for water on Pilkington glass plates were measured for unmodified and modified titania resulting in noticeable shift of absorption spectrum towards lower energy radiation.

*Key words: titanium dioxide, thin films, photoinduced hydrophilicity*

## INTRODUCTION

Titanium dioxide has been widely used, due to its photocatalytic properties, for environmental purification. Another application area pertains to the effect of light on the properties of $TiO_2$-modified surfaces (e.g. self-cleaning glass). Hydrophilicity of $TiO_2$ surface can be induced by UV-irradiation (Wang, et al., 1997). Wang *et al.* (1999) examined changes of contact angles for different liquids on $TiO_2$ single crystals (see Table 1).

Table 1. Contact angles of different liquids on the surface of single $TiO_2$ crystal (Wang et al., 1999)

| $TiO_2$ surface | Contact angles [deg] | | | |
|---|---|---|---|---|
| | Water | Ethylene glycol | Tetralin | Hexadecane |
| Before UV irradiation | 74 | 44 | 12 | 7 |
| After UV irradiation | 0 | 0 | 0 | 0 |

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[*] Department of Chemical Technology, Gdansk University of Technology, 80-952 Gdansk, ul. Narutowicza 11/12, Poland.
[**] Institute of Inorganic Chemistry, University of Erlangen-Nürnberg, 91054 Erlangen, Egerlandstr. 1, Germany.

As a result of UV illumination (40 mW/cm$^2$ for 30 min) of $TiO_2$ surfaces, contact angles of even 0° were reported. While the contact angle for oil did not change too much upon UV illumination, the contact angles for water and ethylene glycol changed significantly. The results of investigations reported in the literature show that contact angles for different liquids decrease during UV irradiation and the value of contact angle depends on time and intensity of irradiation. It was also reported that the light-induced hydrophilic surface can be reversed to a hydrophobic one when the catalyst was kept in the dark for a period of time (Wang *et al.,* 1997; 1999; Miyauchi *et al.,* 2000; 2002; Nakajima, *et al.,* 2001, 2002; Sakai *et al.,* 2001, 2003; Nakamura *et al.,* 2002; Irie *et al.,* 2003; Seki *et al.,* 2004).

## MECHANISM OF PHOTOINDUCTION OF HYDROPHILIC CONVERSION OF TITANIA SURFACE

Wang *et al.* (1998) and Sakai *et al.* (2001) postulated that electrons and holes produced by UV irradiation are trapped by surface and $O^{2-}$ ions, producing $Ti^{3+}$ and oxygen vacancies, respectively. It results in adsorption of water molecules at the defect sites and hydrophilic domains are formed, whereas the rest of the surface remains oleophilic. On long-term storage in the dark, the chemisorbed hydroxyl groups are replaced with oxygen from air to change back the surface properties of $TiO_2$ from hydrophilic to hydrophobic. Presence of $O_2$ blocked the hydrophobic-to-hydrophilic surface wettability conversion. On the other hand, during long-term UV irradiation, when the hydrophilic domain size becomes larger, the oleophilic domain size is smaller. Therefore, the surface becomes relatively hydrophilic and oleophobic when exposed to UV light for a longer time (Wang *et al*., 1999).

## VISIBLE LIGHT-INDUCED HYDROPHILICITY OF TITANIA SURFACE

$TiO_2$ absorbs only UV light, therefore, it should not be possible to obtain hydrophilic properties of unmodified titania surface using visible light. Asahi *et al.* prepared $TiO_{2-x}N_x$ films on which $SiO_2$ was deposited to hold adsorbed water (Asahi, 2001). Their results showed hydrophilic surface of the material which maintained contact angle equal to 6° even after 30 days, contrary to $SiO_2/TiO_2$ film, for which the contact angle gradually increased with time. Irie *et al.* (2003) prepared thin film of $TiO_{2-x}N_x$ without $SiO_2$ deposition. They observed a decrease of water contact angle from 20° to 7° after 4 h irradiation with visible light. The contact angle for unmodified titania film did not change at such conditions. Thus, the hydrophilic properties were enhanced by increasing the degree of nitrogen substitution. A decrease of water contact angle from 25° to 15° as a result of 30 min irradiation of $TiO_{2-x}N_x$ polycrystalline thin film was observed. The hydrophilic conversion was enhanced by applying high anodic potentials. This could be due to efficient charge separation by the anodic potentials and led to better transformation of holes to the titania surface (Premkumar, 2004).

The availability of commercial $TiO_2$ nanofilm, in the form of the Pilkington self-cleaning glass, made it possible to examine the visible light photoinduced hydrophilicity of nitrogen-modified titania films. It is still not clear whether visible light irradiation could influence such phenomenon, similarly to photocatalytic properties of titania.

During research presented in this paper, urea, thiourea and ammonia gas were used to modify with nitrogen commercially-available self-cleaning glass covered with a very thin layer (15 μm) of $TiO_2$. The Pilkington Glass Activ$^{TM}$ represents possible successor to Degussa P-25, especially as a reference for all other photocatalyst films that are being applied for light-enhanced air and water purification, and for self-cleaning purposes (Mills, 2003). Own modification procedure involved dip-coating step (to indroduce nitrogen, carbon and sulphur) using urea and thiourea solutions in water and ethanol. Another modification method was calcination in gaseous ammonia atmosphere.

## EXPERIMENTAL

Glass plates (20x60x5 mm) with a thin layer of $TiO_2$ (15 μm) deposited on one side of $TiO_2$ were obtained from Pilkington (Pilkington Activ$^{TM}$, self-cleaning glass). Similarly to powder catalyst preparation procedure, thiourea, urea and gaseous ammonia were used as the source of nitrogen. The concentration of these compounds was for thiourea: 0.1 M, 1 M; for urea: 1 M, 3 M; and ammonia gas flow: 10 and 45 $dm^3/h$. Ethanol, water and water-ethanol solutions: 1:1, 1:2, 2:1, 1:9, 9:1 were used. The dip-coating technique with 24, 60, 72 mm/min velocity of dipping was applied for the modification using self-made apparatus. Glass plates were washed thoroughly with 2 M NaOH solution and subsequently with distilled water to remove impurities from glass surface. Glass plates were UV pre-irradiated before the dipping procedure. Catalyst samples were heated in air and argon at 250°C to 500°C – for dip-coating procedure from 500 to 600°C when gaseous ammonia was used. Heating a plate without $TiO_2$ layer (blank sample) at 60°C in 2 M NaOH solution was carried out and allowed to remove titania layer completely for reference purposes. The contact angles for water on glass plates were measured by optical goniometer. Oriel 1000 W xenon arc lamp equipped with four optical cut-off filters: $\lambda \geq 320$ nm, 400 nm, 455 nm and 495 nm was the light source. IR radiation was eliminated by water filter which was situated between lamp and cut-off filter. The radiation intensity (power flux) was 800 $mW/cm^2$.

## RESULTS AND DISCUSSION

In order to activate the Plikington glass plates in visible light modification were made. All modified samples were not active in visible light with respect to 4-chlorophenol ($2.5 \cdot 10^{-5}$ M). A noticeable shift of absorption spectra of thin titania layer towards visible light was observed only for a sample modified with 0.1 M thiourea in etanol/water solution (9:1) - see Figure 1. This sample was used in measurements of water contact angles and signed as "modified". The velocity of dipping was fixed at 24 mm/min. After dipping the plate was dried and subsequently heated at 400°C for 15 min in limited access of air.

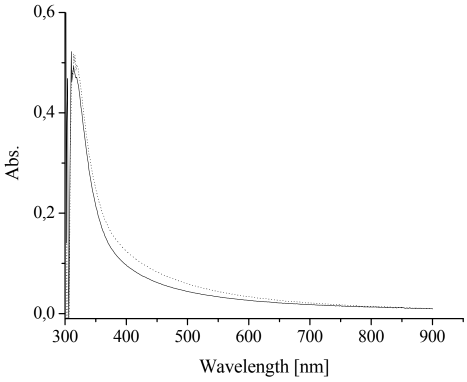

Fig. 1. Absorption spectra of unmodified (solid line) Pilkington titania layer and modified (dotted line)

Glass plates (blank, unmodified and modified) were irradiated for 15 min and 30 min using four cut-off filters: $\lambda \geq 320$ nm, $\lambda \geq 400$ nm, $\lambda \geq 455$ nm and $\lambda \geq 495$ nm. Immediately after irradiation water contact angles were measured. The samples were stored in a dark place for 1 day and water contact angles were measured again. The results of the measurements are shown in Tables 2-5.

Table 2. Results of water contact angle measurements for $\lambda \geq 320$ nm cut-off filter

| Sample | Contact angle [deg] | | | |
|---|---|---|---|---|
| | Initial | Irradiation 15 min | Irradiation 30 min | Storage in dark - 24 h |
| Blank | 61 | 58 | 59 | 58 |
| Unmodified | 58 | 0 | 0 | 54 |
| Modified | 53 | 0 | 0 | 50 |

Table 3. Results of water contact angle measurements for $\lambda \geq 400$ nm cut-off filter

| Sample | Contact angle for water [deg] | | | |
|---|---|---|---|---|
| | Initial | Irradiation 15 min | Irradiation 30 min | Storage in dark - 24 h |
| Blank | 61 | 58 | 57 | 60 |
| Unmodified | 58 | 36 | 25 | 55 |
| Modified | 53 | 27 | 19 | 53 |

Table 4. Results of water contact angle measurements for λ≥455 nm cut-off filter

| Sample | Contact angle for water [deg] | | | |
|---|---|---|---|---|
| | Initial | Irradiation 15 min | Irradiation 30 min | Storage in dark - 24 h |
| Blank | 61 | 60 | 57 | 60 |
| Unmodified | 58 | 40 | 36 | 56 |
| Modified | 53 | 31 | 28 | 51 |

Table 5. Results of water contact angle measurements for λ≥495 nm cut-off filter

| Sample | Contact angle for water [deg] | | | |
|---|---|---|---|---|
| | Initial | Irradiation 15 min | Irradiation 30 min | Storage in dark - 24 h |
| Blank | 61 | 60 | 57 | 60 |
| Unmodified | 58 | 52 | 50 | 54 |
| Modified | 53 | 45 | 41 | 50 |

For both samples (unmodified and modified), after UV illumination (λ≥320 nm) the contact angles decreased to 0° for two irradiation times contrary to glass plate without titania layer (blank sample), which is consistent with data available in the literature, pertaining to the Pilkington glass (Mills, 2003). Therefore, strong photoinduced hydrophilic effects of titania surface has a strong evidence for such a range of irradiation. After 1-day storage in dark the contact angles returned to almost initial values. The elimination of UV range using λ≥400 nm cut-off filter resulted in significantly greater values of water contact angle after irradiation. For unmodified titania layer the contact angle decreased from 58º to 36º (28 % of contact angle decrease) and 25º (57 %) after 15 and 30 min of irradiation. For the modified sample, a clear improvement was observed, not resulting from the experimental error: 53º to 27º (49 %) and 19º (64 %). For λ≥455 nm cut-off filter the hydrophilic effect was smaller, especially the difference between 15 and 30 min of irradiation contained in experimental error. After 15 min of irradiation contact angles were comparable to that obtained for the cut-off filter used previously. Modification of catalysts did not result in a significant increase of the hydrophilic effect in this case. Restriction of light range to 495 nm resulted in a very small decrease of contact angles for both samples. For the modified sample contact angle decreased from 53º to 41º (23 %), and for unmodified from 58º to 51º (12 %) after 30 min of irradiation.

## CONCLUDING REMARKS

For the first time titania coating on the Pilkington Glass Activ$^{TM}$ was modified with non-metal elements (nitrogen, carbon, sulphur) using thiourea as precursor. A small shift in the absorption spectrum was observed. The change in optical properties of the thin film is probably responsible for improvement of hydrophilic properties in comparison with unmodified sample under visible light irradiation.

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Cienkie filmy tlenku tytanu (IV) mogą być używane szczególnie jako komponent szkieł samoczyszczących wykorzystując zjawisko fotoindukowanej hydrofilowości powierzchni $TiO_2$. Po raz pierwszy cienka warstwa $TiO_2$ znajdująca się na powierzchni Pilkington Glass Activ$^{TM}$ została poddana modyfikacji za pomocą amoniaku, tiomocznika i mocznika w celu wprowadzenia pierwiastków niemetalicznych do struktury $TiO_2$ aby przesunąć widmo absorpcji w kierunku światła widzialnego. Kąty zwilżania dla wody zdemineralizowanej płytek szklanych Pilkington zostały zmierzone dla próbki niezmodyfikowanej i zmodyfikowanej, która odznaczała się zauważalnym przesunięciem spektrum absorpcyjnego w kierunku promieniowania o mniejszej energii.