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Effect of glass substrate and deposition technique on the properties of sol gel TiO_2 thin films

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ABSTRACT

Na^+ ions have a detrimental effect on the photocatalytic activity of thin sol gel films deposited on soda lime glass due to their diffusion into the film during the calcination process. Given that the content of sodium in glass substrate might be the crucial parameter in determining the activity of a photocatalyst, the aim of the present work was the comparison of the photoinduced properties of a thin TiO_2 film prepared on three different glass substrates namely on quartz (Q) glass, borosilicate (BS) glass and soda lime (SL) glass which have different sodium content. The prepared layers were characterised by X-ray diffraction and UV–vis spectroscopy. The diffusion of Na^+ from the substrate into the layers was determined by Glow Discharge Atomic Emission Spectroscopy. The photocatalytic activities of the films were assessed using two model pollutant test systems (resazurin/resorufin ink and stearic acid film), which appeared to correlate reasonably well. It was observed that TiO_2 layer on SL glass has a brookite crystalline structure while the TiO_2 layer on BS and Q glass has an anatase crystalline structure. On the other hand, the photodegradation of the model dye on TiO_2 films deposited on Q and BS glass is about an order higher than on SL glass. The low sodium content of BS glass makes it the most suitable substrate for the deposition of photoactive sol gel TiO_2 films.

1. Introduction

At present, thin transparent TiO_2 films deposited on glass posses high application potential based on its easy cleaning properties, which are due to its ability, upon UV irradiation to degrade solid organic impurities and to form a superhydrophilic surface. It has been reported that Na^+ ions in soda lime glass have a detrimental effect on the photocatalytic activity of deposited sol–gel thin films [1–3] due to their diffusion into the photocatalytic film during calcination step. Paz and Heller [1] report that at high concentrations sodium ions prevent formation of the photoactive anatase phase and, at low concentrations introduce surface and bulk recombination centers. However, Nam et al. [3] claim that the above recombination centre hypothesis [1,4] does not hold for the sol gel layers, but instead, suggest that the Na^+ ions effect the photocatalytic activity of the titania film by changing the particle size of anatase (see Table 1).

The influence of Na^+ ions on the photocatalytic activity of resulting TiO_2 powders has been studied via the addition of NaOH to sol gel precursors. It was found that Na^+ ions prevent the formation of anatase crystals and the transformation to rutile [5]. When a hydrothermally prepared TiO_2 colloidal sol, to which NaOH was added, was used to create a TiO_2 powder, the product was titania in its less common brookite crystal phase [6].

The negative effect of Na^+ ions can be suppressed by the formation of thin proton exchange layer (created usually by etching the glass substrate in concentrated acid) [1] or via the introduction of a SiO_2 barrier layer between the glass substrate and the thin TiO_2 film [2,7–9]. Using SiN_x as barrier layer was found even more efficient then SiO_2 [10]. In our previous work [11] using Glow Discharge Atomic Emission Spectroscopy (GDS), the Na^+ concentration profile was determined in TiO_2 films deposited onto soda lime glass and on soda lime glass precoated by SiO_2 layer. The presence of Na^+ ions in the titania film was only identified in the first case and the second case had a markedly higher photocatalytic activity. These results proved not only the effectiveness of the SiO_2 barrier layer, but also the negative effect of Na^+ ions in a titania film on its photoactivity.

It is important to mention that the content of sodium is not the same for all types of glass. In the previous comparative studies only glass substrates with or without Na^+ were investigated [1–3,7–11]. Furthermore in each study only one photocatalytic system was chosen to assess the activity of the titania film. Therefore, the aim of the present work is the comparison of photocatalytic properties of

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Table 1
Properties of TiO_2 films (thickness, crystalline structure, crystal size) deposited on various substrates.

Substrate	Deposition	Thickness/nm	Crystal phase	Crystal size/nm
Quartz	Dip coating	69	Anatase	17 ± 4
Borosilicate	Dip coating	75	Anatase	23 ± 3
Soda lime	Dip coating	160 (2 layers)	Brookite	50 ± 2
Quartz	Spin coating	140	Anatase	18 ± 2
Borosilicate	Spin coating	124	Anatase	21 ± 2
Soda lime	Spin coating	150	Anatase	50 ± 2

thin TiO_2 film prepared on three different glass substrates, namely on quartz glass (Q), borosilicate glass (BS) and soda lime glass (SL), each of which has a different Na_2O contents.

2. Experimental

2.1. Film preparation

In the preparation of sol–gel TiO_2 films, titanium isopropoxide (TiP, Sigma Aldrich) was used as a precursor, propan-2-ol (IPA) and acetylacetone (AcAc) served as solvents (both HPLC grades) and hydrochloric acid was used as a catalyst. The molar ratio of TiP to HCl was 20 and molar ratio of TiP to the sum of the solvents (IPA and AcAc) was 0.1. All the components (precursor, solvent and catalyst) were mixed for 3 h at room temperature (22 °C).

The prepared sols were deposited on the surface of glass substrates using dip coating and spin coating techniques. Three types of glass substrates were used namely quartz glass (Q) with 99% of SiO_2 (Newcastle Optics, 25 mm in diameter, 1 mm thickness), borosilicate glass (BS) with 80% of SiO_2 and 5% of Na (VWR international, 24 mm in diameter, 0.1 mm thickness) and soda lime glass (SL) with 70% of SiO_2, 15% of Na and 10% of Ca (Marienfeld, 25.4 mm × 76.0 mm, 1.1 mm thickness).

The dip-coating was performed at room temperature (22 °C). The immersion rate, the holding time in the sol and the withdrawal rate were initially optimized and then kept constant for all experiments: i.e., 20 cm min^{-1}, 30 s and 6 cm min^{-1}, respectively. The spin coating was performed as follows. 4 drops of sol were placed on the surface substrates under rotation 1000 rpm for 20 s. Finally, the coated substrates were dried for 30 min at room temperature (22 °C). It was previously found by DTA/TG analysis of TiO_2 xerogel (liquid sol dried at room temperature (22 °C) for about five days) that above the level of 500 °C there is no significant loss of mass with increasing temperature [11]. Thus calcination at temperature at 500 °C (air; atmospheric pressure; rate of temperature rise 3 °C/min) for 2 h was used as final treatment of sol–gel precursors deposited on glass substrates. All films appeared smooth and optically transparent.

2.2. Layer characterization

The surface morphology and the thickness of the layers were evaluated with help of SEM (Hitachi S4700) and profilometry (Alpha Step 500), respectively. The location and presence of characteristic diffraction lines were observed by X-ray diffractometer (Seifert – XRD 3000; Panalytical HighScore Plus). These data were also used to estimate the crystalline size. The light absorption properties of the layers were evaluated by UV-Vis spectrophotometer Cary 100. The diffusion of Na^+ from the substrate into the layers was determined by Glow Discharge Atomic Emission Spectrometer (GDS; Horiba GD-Profiler 2).

2.3. Photoinduced properties

The photocatalytic activities of the films were assessed using two model test systems, namely: resazurin (Rz)/resorufin (Rf) [12–14] and stearic acid [14,15]. In both cases the films were irradiated with six 8 W black light bulbs (maximum at 350 ± 20 nm) contained in a semicylindrical lamp holder with an aluminium reflector and held 10 cm above the samples. The mean incident photon flux onto the substrates was 1.9 mW cm^{-2} as measured using UVX radiometer, UVP, USA.

The resazurin ink comprised of 3 g of 1.5 wt% aqueous solution of hydroxymethylcelulose (HEC), 0.3 g of glycerol and 4 mg of Rz. A film of ink was spun coated on the surface of substrate (4 drops of ink, 500 rpm for 15 s) and dried in an oven at 70 °C for 10 min. A typical dry ink has thickness about 590 nm when coated in the above manner onto glass or non-porous transparent TiO_2 film. UV–vis spectrum of the transparent, Rz ink-coated, film was measured as a function of irradiation time. The absorbance of the film at 619 nm is proportional to the concentration of Rz dye present, whereas the absorbance at 588 nm is proportional to the amount of Rf produced.

Stearic acid was also deposited on the surface of transparent film by spin coating (7–10 drops of stearic acid (SA) solution in chloroform (30 g/l), 500 rpm for 15 s), then 30–60 s drying at 100 °C (chloroform removal). The amount of SA on the surface of the titania photocatalyst film was determined using FTIR spectroscopy (1600 FTIR, Perkin Elmer, UK), via the integrated absorbance of stearic acid between 2700 and 3000 cm^{-1}; the recent reported proportionality constant of 9.7×10^{15} stearic acid molecules per cm^2 per integrated absorbance unit over 2700–3000 cm^{-1} [15] was used in this work, which is around three times higher than the value estimated by Paz et al. [16]. The rate of photocatalytic mineralisation of SA was determined by measuring the change in concentration of SA as a function of irradiation time.

3. Results and discussion

3.1. AFM, XRD and Raman analysis

The TiO_2 layers prepared on various glass substrates were examined using a number of different characterization techniques. The surface roughness of all the films, as assessed by AFM was generally very low. As an example, the AFM image of sol gel TiO_2 film prepared by dip coating on quartz glass support is shown in Fig. 1. AFM images of films on soda lime glass and borosilicate glass were similar with the rms parameter around 1 nm.

X-ray diffraction patterns of the TiO_2 films deposited by spin coating and dip coating on three supports are shown in Figs. 2 and 3, respectively. TiO_2 films prepared by *spin coating* have anatase crystalline structure for all the used substrates although the crystallinity of such films on BS and Q substrate is much higher than that on the SL substrate (see Fig. 2). In contrast, titania films deposited by *dip coating* revealed an anatase phase for the titania film on BS and Q glass but no crystallinity on SL glass (see Fig. 3). Further work revealed that whereas the first layer of titania deposited onto SL glass was amorphous, further dip coats produced films of increasing thickness that only appeared to have the less common brookite crystal phase present (see Fig. 4). Raman spectroscopy confirmed these findings.

These finding appear to confirm previous observations that the presence of sodium ions in the supporting substrate acts as an

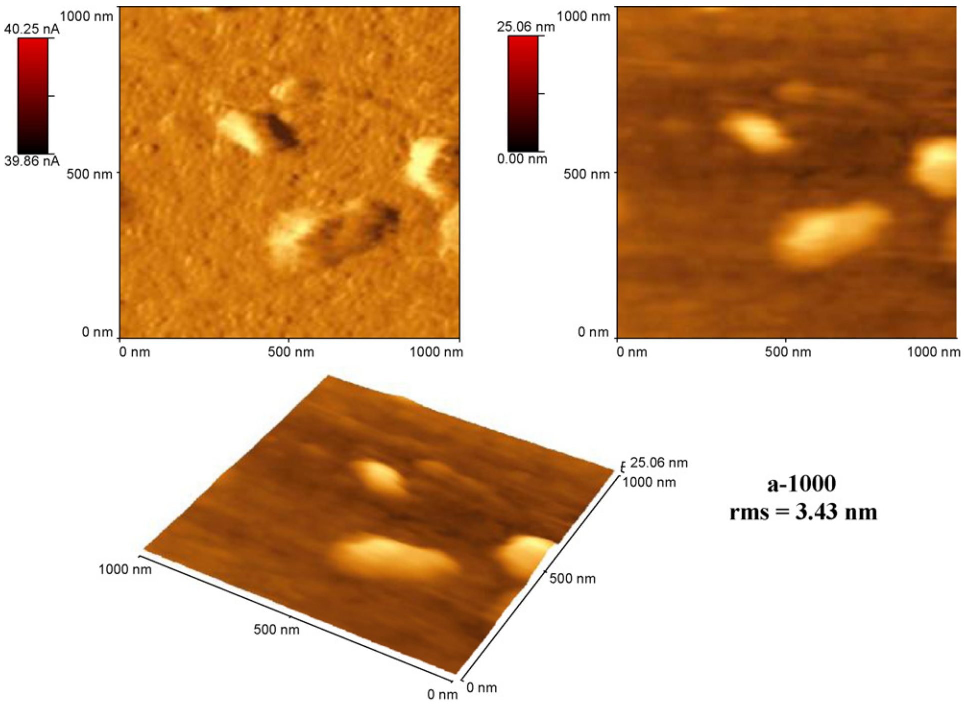


Fig. 1. AFM image for sol gel TiO_2 film prepared by dip coating on quartz glass support.

inhibitor to crystallisation and promotes the formation of the less common brookite phase of titania. It is not clear why spin-coated films on SL glass only show an anatase phase, although they are much thicker (150 nm compared to (typically) 80 nm) and so the level of Na^+ in spin-coated films on SL will be much lower than that in dip-coated film on SL. The higher the level of Na^+, the greater the likelihood of brookite formation.

3.2. *Depth profiles of the titania films on different glasses*

Concentration profiles for various elements (Na, Ca, Al, Si, B, O and Ti) were recorded for typical films on the different glass types and the main results are illustrated in Fig. 5a–c. In each diagram the vertical line represents the interface between the TiO_2 film and the glass support and was constructed on the basis of the Ti profile. The layer thickness thus can be related to the sputtering time at the cross section of vertical line and *x*-axis. But due to the different material properties of individual substrates, the relation between sputtering time and layer thickness is different for each substrate.

From Fig. 5a it is evident that Na and Ca are present in TiO_2 film deposited on SL glass. The highest amount is on the interface between glass and TiO_2 film but a significant amount is also in the film. The average Na concentration in TiO_2 film determined from GDS analysis (Fig. 5a) is ≈20%. This is significantly higher than bulk concentration of Na in glass substrate (15%). Nam et al. [3] analysed the ca 2 nm surface layer of sol–gel TiO_2 thin films deposited on various glass substrates and heated at 500 °C and found that in the case of crown glass (11% of Na_2O) the surface layer contains 11% of Na while in the case of crown glass coated with SiO_2 layer the surface layer contained only 3.5% of Na. Crown glass has a similar composition to that of the soda lime glass used in this study. The present results concerning soda lime glass as substrate are thus consistent with data of Nam et al. [3] but show also the significant presence of Ca in TiO_2 film.

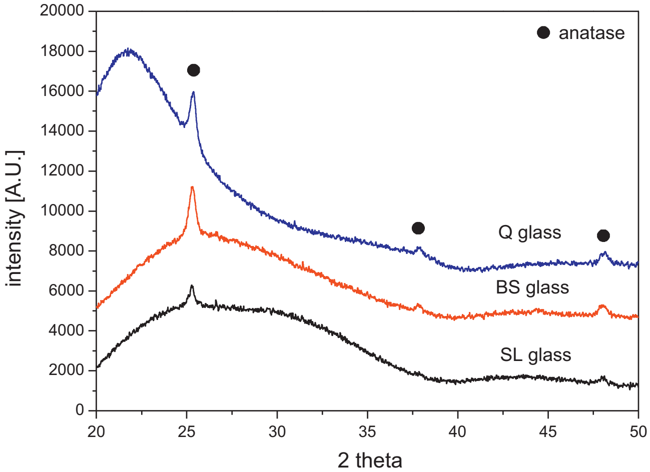


Fig. 2. X-ray patterns of 1 layer TiO_2 films prepared by spin coating on three glass substrates (anatase; PDF number 071-1166). Thickness around 150 nm.

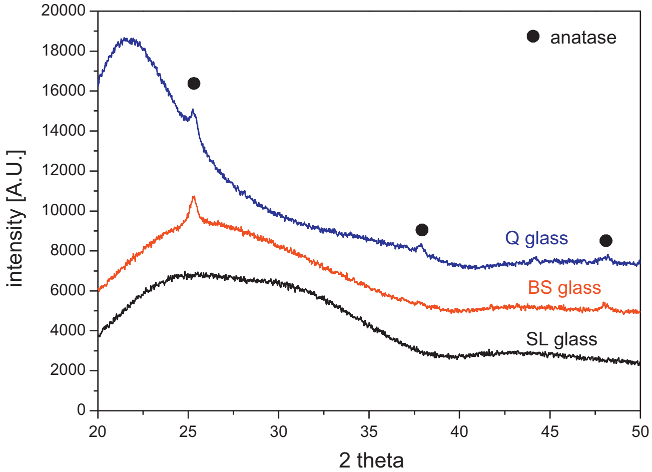


Fig. 3. X-ray patterns of TiO_2 films prepared by dip coating on three glass substrates (anatase; PDF number 071-1166). Thickness around 80 nm.

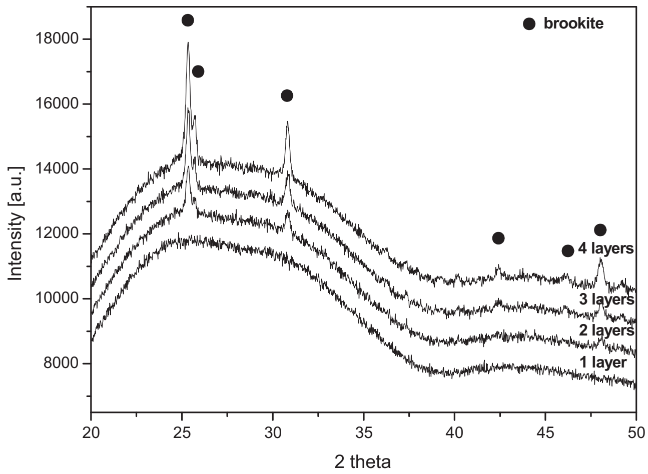


Fig. 4. X-ray patterns of TiO_2 films prepared by dip coating on soda lime glass substrate. Thickness of 1, 2, 3, 4 layer film is 80, 160, 260 and 360 nm, respectively (brookite, PDF number 075-1582).

On the other hand Fig. 5b shows that even though B and Si are present in BS glass their content in TiO_2 film is negligible. Na is present only at the interface between TiO_2 layer and glass substrate and the average Na concentration in TiO_2 film determined from GDS analysis (Fig. 5a) is only 0.2%. Similarly a low average content of Na was calculated for dip coated TiO_2 film deposited on glass substrate covered by SiO_2 barrier layer (0.2% [20]).

The fact that the diffusion of B from borosilicate glass to TiO_2 film is insignificant is not surprising, but the almost negligible amount of Na^+ in the TiO_2 films deposited on borosilicate glass means that Na^+ diffusion in such glass is suppressed even at elevated temperatures above 400 °C.

Pay and Heller [1] report that a one layer TiO_2 film has higher percentage of sodium compared with a two layer TiO_2 film. Films were prepared by spin coating with only a drying step between subsequent layer deposition with final calcination at 400 °C. As shown in Fig. 5a the sodium tends to accumulate at the glass–TiO_2 interface and at the TiO_2–air interface (reported also in [1]). This means that the amount of leaching into the TiO_2 layer should depend not on the thickness but instead on the temperature (with its exponential effect on the diffusion coefficient) and on the calcination time. Temperature and time was equal in both cases (dip and spin coating) hence the amount of sodium should be similar, which means that the average concentration (which is responsible for preventing anatase formation) is expected to be lower in the case of the thicker layer. Thus, the reason for different behaviour of spin and dip coated films is not in the technique itself (they are very similar and differ only by the forces acting to reduce the thickness, i.e. centrifugal vs. gravitational) but the fact that 1 layer of spin coated film was two times thicker and thus the resulting concentration of sodium after calcination was lower. The situation is different when we compare films of the similar thickness (160 nm) prepared by dip and spin coating. Here the calcination time is two times higher for dip coated film (the calcinations step was performed after each layer deposition) which results in two times higher amount of sodium in the film.

3.3. Photocatalytic reduction of resazurin and oxidation of stearic acid

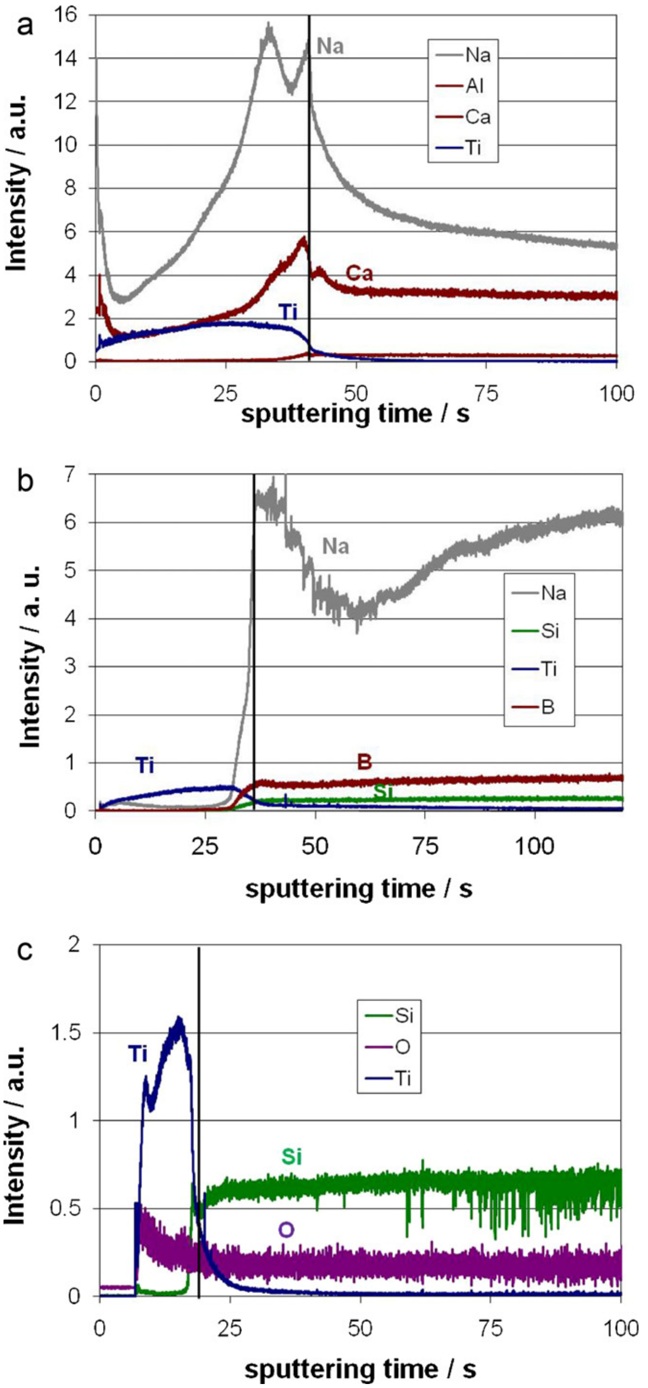


Fig. 5. (a) GDS profile for TiO_2 layer prepared by spin-coating on sodalime glass. Signal for B, Al, and Si was negligible. (b) GDS profile for TiO_2 layer prepared by spin-coating on borosilicate glass. Signal for Ca was negligible. (c) GDS profile for TiO_2 layer prepared by spin-coating on quartz glass. Signal for Na and Ca was negligible.

The resazurin ink works by placing the dye and a sacrificial electron donor, glycerol, onto the surface of the photocatalyst material under test, in this case titania. Upon UV irradiation of the titania, electron–hole pairs (e^-h^+) are generated and those that are able to migrate to the surface are able to reduce Rz (blue) to Rf (pink) and simultaneously oxidised the glycerol to glyceraldehyde and then onto glyceric acid. These reactions and an overall reaction scheme are illustrated in Eqs. (1)–(3). This method has the major advantage over most methods in that it is very fast and easy to use and requires no sophisticated analytical equipment to assess the presence and relative activity of a photocatalytic material [13,17].

$$\text{Glycerol} + h^{*} \rightarrow \text{Glyceric acid} \qquad (1)$$

$$\text{Rz} + e^{-} \rightarrow \text{Rf} \qquad (2)$$

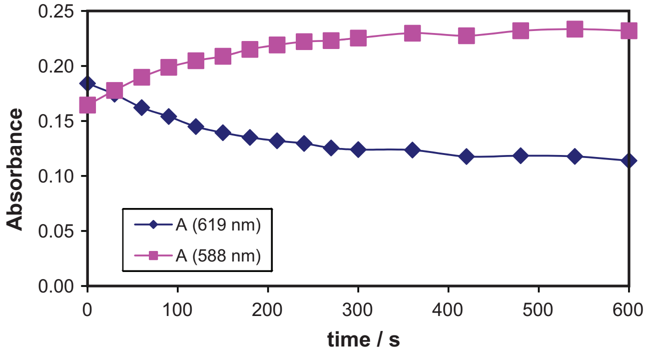
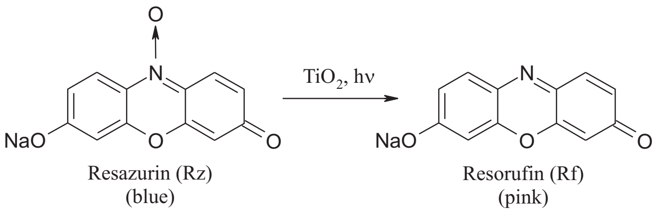


Fig. 6. Time dependence of absorbances at 619 and 588 nm corresponding to Rz decrease and Rf increase during irradiation of TiO_2 film prepared by spin coating technique on soda lime glass (SL).



(3)

The typical observed variations in the absorbances due to the disappearance of Rz (monitored at 619 nm) and concomitant appearance of Rf (monitored at 588 nm) for an Rz ink on a single layer on TiO_2 produced by spin coating on SL glass is illustrated in Fig. 6. This method was used to test all the TiO_2 on glass films and the measured initial rates of change (absorbance units per s) in the Rz absorbance as a function of irradiation time are summarised in Table 2.

In contrast, in the stearic acid test the overall reaction is the photocatalytic mineralization of SA which can be summarised as follows:

$$CH_3(CH_2)_{16}CO_2H + 26O_2 \xrightarrow{TiO_2} 18CO_2 + 18H_2O \qquad (4)$$

The destruction of SA as a function of irradiation time was monitored by FTIR spectroscopy (i.e. integrated absorbance of stearic acid in the range 2700–3000 cm^{-1}) and the variations in this area as a function of time for TiO_2 films prepared by spin coating on three glass supports are shown in Fig. 7. From these results it is evident that layer prepared on SL glass exhibits a negligible decrease of the amount of stearic acid. For comparison of TiO_2 layers deposited on various substrates initial slopes, R_i ($A\,cm^{-1}\,min^{-1}$), were calculated and shown in Table 2.

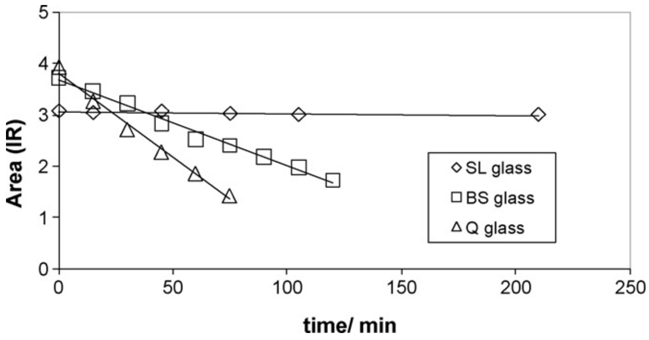


Fig. 7. Dependence of integrated area under FT-IR absorbance spectra from 2700 cm^{-1} to 3000 cm^{-1} of a film of stearic acid on TiO_2 film prepared by spin coating on various glass substrates. SL, soda lime; BS, borosilicate; Q, quartz.

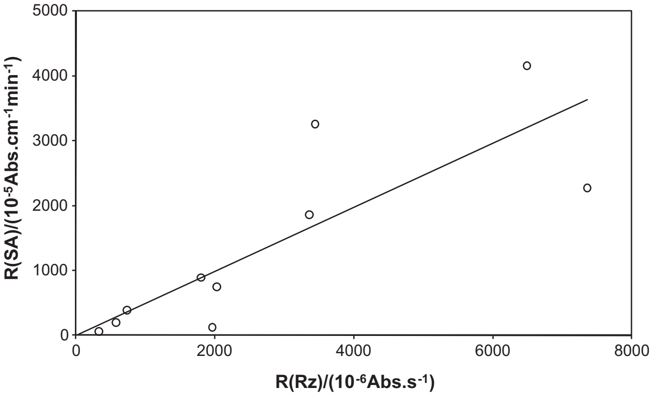


Fig. 8. Rate of stearic acid destruction (R(SA)) versus rate of Rz reduction (R(Rz)) for all samples tested which exhibited activity for both tests.

From Table 2 it is clear that the Rz test can detect some photocatalytic activity, albeit very small) in some samples (SL 2 layers by dip-coating), where SA cannot. A plot of the rate of SA removal versus the rate of Rz reduction for all samples is illustrated in Fig. 8 and shows an otherwise reasonable degree of correlation between the two tests. A similar correlation for these two tests has been observed elsewhere using samples of TiO_2 on glass produced by CVD [12].

Analysis of the results in Table 2 reveal the not surprising result that the higher the Na^+ content of the glass the poorer the photocatalytic activity of the titania photocatalyst. The low pho-

Table 2
Summary of photodegradation experiments.

Deposition	Substrate	No. of layers	Thickness (nm)	Initial slopes of degradation, R_i	
				Rz ($A\,s^{-1}$)	SA ($A\,cm^{-1}\,min^{-1}$)
Dip coating	Soda lime	1	80	Not detectable	Not detectable
		2	160	0.000195	Not detectable
		3	260	0.000577	0.00198
		4	360	0.001964	0.00120
	Borosilicate	1	75	0.002027	0.00750
	Quartz	1	69	0.001797	0.00890
Spin coating	Soda lime	1	150	0.000329	0.00060
		2	320	0.000736	0.00390
	Borosilicate	1	124	0.003360	0.01860
		2	290	0.007358	0.02270
	Quartz	1	140	0.003443	0.03260
		2	310	0.006490	0.04160

toactvivity of TiO_2 layers on soda lime glass cannot be explained by the presence of brookite, since brookite has been reported by Addamo et al. [18] and Di Paola et al. [19] as being photocatalytically active. Thus, it is not the presence of brookite but the high content of Na that is responsible for low photoactivity of resulting TiO_2 film.

The efficient suppression of Na^+ diffusion during a calcinations step can be achieved by introducing either a barrier SiO_2 layer (as demonstrated by GDS measurements [20]) or by using borosilicate glass as a substrate. Borosilicate glass is substantially more expensive than soda lime glass and this should be taken into account when deciding the most appropriate glass support.

4. Conclusions

The deposition technique can have a strong influence on the crystalline structure of titania films deposited on SL glass. In the case of layer prepared by dip coating the thickness is much smaller and thus the amount of Na^+ ions in the dip coated film (due to the diffusion of Na^+ from substrate) is higher than in spin coated film. As a result the content of Na^+ is high, rendering anatase unstable and leading to the formation of a brookite phase. The photocatalytic activities of TiO_2 films on Q and BS glass are similar, for 1 layer dip coated films, but is much smaller on SL glass. Depth profile elemental analysis of these films confirms the presence of Na and Ca in TiO_2 film on soda lime glass substrate while in the case of borosilicate glass neither Na nor B is present in TiO_2 film. The low sodium content of borosilicate glass makes it the most suitable substrate for the deposition of photoactive sol gel TiO_2 films.

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References

[1] Y. Paz, A. Heller, J. Mater. Res. 12 (1997) 2759–2766.
[2] T. Watanabe, S. Fukayama, M. Miyauchi, A. Fujishima, K. Hashimoto, J. Sol–Gel Sci. Technol. 19 (2000) 71–76.
[3] H.-J. Nam, T. Amemiya, M. Murabayashi, K. Itoh, J. Phys. Chem. B 108 (2004) 8254–8259.
[4] J.-M. Herrmann, H. Tahiri, Ch. Guillard, P. Pichat, Catal. Today 54 (1999) 131–141.
[5] H.-J. Nam, T. Amemiya, M. Murabayashi, K. Itoh, Res. Chem. Intermed. (2005) 365–370.
[6] S.-J. Kim, K. Lee, J.H. Kim, N.-H. Lee, S.-J. Kim, Mater. Lett. 60 (2006) 364–367.
[7] K. Doushita, T. Kawahara, J. Sol–Gel Sci. Technol. 22 (2001) 91–98.
[8] K. Funakoshi, T. Nonami, J. Am. Ceram. Soc. 89 (2006) 2782–2786.
[9] M. Addamo, V. Augugliaro, A. Di Paola, E. Garcia-Lopez, V. Loddo, G. Marci, L. Palmisano, Thin Solid Films 516 (2008) 3802–3807.
[10] E. Aubry, M.N. Ghazzal, V. Demange, N. Chaoui, D. Robert, A. Billard, Surf. Coat. Technol. 201 (2007) 7706–7712.
[11] P. Novotna, J. Krýsa, J. Maixner, P. Kluson, P. Novak, Surf. Coat. Technol. 204 (2010) 2570–2575.
[12] A. Mills, J. Wang, S.-K. Lee, M. Simonsen, Chem. Commun. (2005) 2721–2723.
[13] A. Mills, J. Wang, M. McGrady, J. Phys. Chem. B 110 (2006) 18324–18331.
[14] A. Mills, M. McFarlane, Catal. Today 129 (2007) 22–28.
[15] A. Mills, J. Wang, J. Photochem. Photobiol. A: Chem. 182 (2006) 181–186.
[16] Y. Paz, Z. Luo, L. Rabenberg, A. Heller, J. Mater. Res. 10 (1995) 2842–2848.
[17] J. Zita, J. Krýsa, A. Mills, J. Photochem. Photobiol. A: Chem. 203 (2009) 119–124.
[18] M. Addamo, M. Bellardita, A. Di Paola, L. Palmisano, Chem. Commun. (2006) 4943–4945.
[19] A. Di Paola, M. Addamo, M. Bellardita, E. Cazzanelli, L. Palmisano, Thin Solid Films 515 (2007) 3527–3529.
[20] J. Zita, J. Maixner, J. Krýsa, J. Photochem. Photobiol. A: Chem. 216 (2010) 194–200.