

Scientific paper

Enhancement of Photocatalytic Activity of Sol-gel TiO₂ Thin Films With P25

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Dedicated to the memory of Professor Ljubo Golič

Abstract

Semi-transparent TiO₂ thin films were prepared via sol-gel method using TiCl₄ as a precursor with an addition of various loadings of Degussa P25 powder. Thus prepared thin films were dip-coated on substrates, air dried and heat treated for 30 minutes at 500 °C to obtain uniform films with good adhesion to the substrate. Different substrates were used: SiO₂-coated soda-lime glass for photocatalytic experiments, aluminum foil for TG measurements and platinum foil to investigate the adhesion to various substrates. Thin films and the xerogels prepared from sols were characterized by different techniques, e.g. thermogravimetric (TG) analysis, differential scanning calorimetry (DSC), X-ray diffraction (XRD), UV–Vis spectroscopy, scanning electron microscopy (SEM), Fourier transform infrared (FT–IR) spectroscopy and contact angle measurements.

The addition of commercial TiO₂ P25 powder significantly increased the photodegradation rate of an aqueous solution of azo dye Plasmocorinth B, which was proved by *in-situ* UV–Vis spectroscopic measurements of the dye solution.

Keywords: TiO₂ thin films, TiCl₄ precursor, sol-gel, peroxo-modified sol, Degussa P25, photodegradation.

1. Introduction

Photocatalysis is becoming increasingly attractive for both fundamental science and practical applications. TiO₂ photocatalyst has become the material of choice in the destruction of recalcitrant organic pollutants in water and air, sterilizing, self-cleaning processes, etc.^{1,2}

The principle of semiconductor photocatalytic reaction is simple. Irradiation of the semiconductor with light having the energy equal to or greater than the corresponding bandgap (separating the vacant conduction band, CB, and the filled valence band, VB) excites an electron from the VB to the CB to form an excited electron (e⁻) – positive hole (h⁺) pair. These e⁻ and h⁺ reduce and oxidize, respectively, the chemical species on the surface of the photocatalyst, unless they recombine to give no net chemical reaction but heat. Recombination of e⁻ and h⁺ is the most frequent process and the success of photocatalytic reaction actually depends on successful diminishing of the recombination process.

Generally, TiO₂ photocatalyst is used in two forms: as highly dispersed fine particles or in immobilized form on a substrate. Aqueous suspensions of TiO₂ are mostly used for photocatalysis, since the immobilization of TiO₂ on solid supports reduces its photocatalytic activity. However, the major problem with suspensions is the particle–fluid separation after the completion of photocatalytic process, which is almost impossible on a large scale.

Sol-gel methods, including dip or spin coating as a final step of preparation, have been extensively used to prepare various kinds of metal oxide thin films.^{3,4} These processes are relatively cheap, and various substrates can be used. Using this technique TiO₂ films of high photocatalytic activity have been produced.^{5–7}

Sols from TiCl₄ are alkaline which makes them applicable for metal surfaces. Synthesis at higher temperatures yields sols containing anatase⁸ and the reagent itself is inexpensive.

By majority the sols from organometallic precursors are acidic which limits the use of metals as a substrate in this system. It has been reported that aluminum and platinum foils are effective substrates for thermal analysis on thin films, since thermal analysis of thin films is a demanding procedure and direct measurements of thin films are still not very common.^{9,10} Because of the enormous dilution effect caused by the massive substrate, the observed mass changes are in the range of buoyancy and aerodynamic effects.

Ichinose et al. synthesized peroxo-modified anatase sol using peroxotitanium acid (PTA) solution.⁸ This method has many advantages compared to the common sol-gel methods. Regardless of all the advantages, the PTA solution is derived from TiCl_4 aqueous solution, which limits the reaction temperature to ca. 0°C due to the highly exothermic reaction. Unfortunately reaction temperature of 0°C is difficult to implement at a large-scale level. Yuan et al. reported on the preparation of PTA solution by deriving it from TiCl_4 /ethanol/water solution at room temperature.¹¹ Balasubramanian et al. prepared thin films from alkoxide sol using a P25 powder-modified sol-gel method. Their films exhibited enhanced photocatalytic activity and improved hardness over those obtained by using conventional alkoxide sol-gel procedure.^{12,13}

It is known that immobilized TiO_2 has lower photocatalytic activity than aqueous suspensions of TiO_2 due to smaller surface area. The purpose of our study was to enhance photocatalytic activity of TiO_2 thin films. We investigated the influence of the addition of commercially available TiO_2 P25 powder (Degussa) on the photocatalytic activity and adhesion to the substrate by preparing thin films via a sol-gel method using TiCl_4 as a precursor. The prepared sols were alkaline which enables various metal substrates to apply in the system. The addition of P25 into the sol significantly increased the photocatalytic activity and hydrophilicity of thus prepared thin films.

The optical properties and structure of the material were investigated by UV–Vis spectroscopy, Fourier transform infrared (FT–IR) spectroscopy, scanning electron microscopy (SEM), thermogravimetric (TG) analysis, differential scanning calorimetry (DSC) and X-ray diffraction (XRD) analysis, while photoefficiency of thin films was determined by *in-situ* UV–Vis spectroscopy. Viscosity of primary sol without P25 loading was estimated by the capillary flow method. The photocatalytic activity of thin films with different loadings of P25 was studied. The aqueous solution of Plasmocorinth B was used as a photo-degradation medium since in the absence of photocatalyst and under UVA radiation this azo dye is very stable.¹⁴

2. Experimental

2.1. Preparation of Sols and Xerogels

0,1 mol of titanium(IV) tetrachloride (Fluka) was dissolved in 3,4 mol of ethanol and then 300 mL of water

was added. 25% solution of ammonia (TKI) was added to titanic acid solution until the pH value reached 9. The precipitate was rinsed with distilled water and centrifuged several times until no Cl^- ions could be detected anymore. Then the gel was dissolved in 30% hydrogen peroxide (Belinka) to get a transparent orange sol of titanium peroxo complex. The sol was diluted with water to obtain suitable viscosity for the deposition of films (approx. 80 cP). The viscosity of thus prepared sol was estimated by capillary flow method. The process is shown in details in the flow chart (Figure 1).

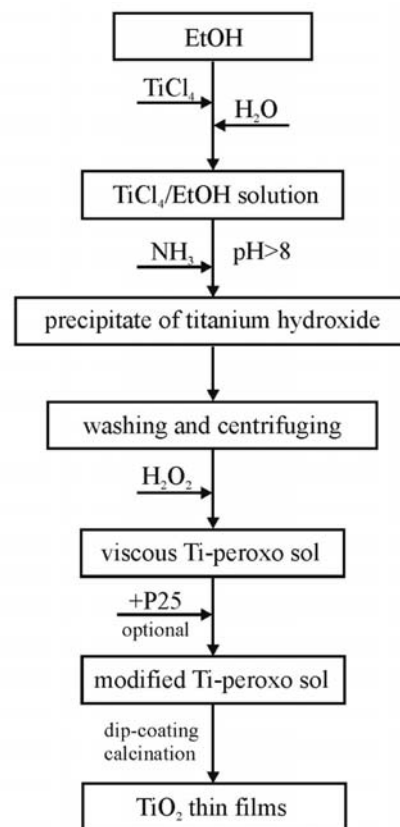


Figure 1. Flow chart for the preparation of TiO_2 thin films.

Commercial nanophase TiO_2 Degussa P25 powder ($50\text{ m}^2/\text{g}$; 15–30% rutile + 85–70% anatase, mean diameter of 30 nm) was used for preparing modified sols (see Table 1). The powder was slowly added into the peroxo sol under vigorous stirring. Modified sols of different concentrations of P25 were prepared (5–30 g/L) and appeared as thick, light yellow suspensions. Before the deposition of thin films the modified sol was stirred rapidly for a few hours and then ultrasonicated for half an hour to prevent agglomeration.

A xerogel of the primary sol was prepared by placing the gel in a Petri dish and drying it in air at ambient temperature.

Table 1. Prepared samples and contents of P25

Thin Film	0	5P25	10P25	20P25
P25 loading	/	5 g/L	10 g/L	20 g/L

2. 2. Preparation of Thin Films

Soda-lime glass plates (75 mm × 25 mm × 1 mm) were used for the deposition of films. The plates were cleaned thoroughly with ethanol and distilled water in an ultrasonic bath for 5 minutes and dried before deposition. In almost all cases SiO₂ protecting layer (~ 150 nm) was deposited from SiO₂ sol which was prepared according to Černigoj et al.¹⁵. Soda-lime glass with no protecting layer was used to compare influence of SiO₂ protecting layer on light absorption properties and on photocatalytic activity of the thin films. After the deposition of SiO₂ layer, a wetting agent (1 wt. % of Etolat (C₁₃H₂₇-O(CH₂-CH₂-O)₆-H produced by Teol, Slovenia) in distilled water) was dispersed on the substrate which was then dipped in the viscous sol and pulled out with a uniform pulling rate of 5 cm/min using the dip-coating technique. The resulting thin film of TiO₂ was first dried in air at room temperature and then calcined at 500 °C. The thickness of the films was increased by repeating the dipping and heat-treatment cycles. Between two subsequent coatings, films were calcined for 15 minutes at 500 °C and after four coatings the calcination time was 30 minutes. Thin films were deposited on aluminum foil for TG measurements and on platinum foil to investigate the adhesion to various substrates. Before deposition the same procedures as for glass plates were used.

2. 3. Characterization of the Thin Films and Xerogels

The crystallinity of TiO₂ xerogels was identified using a PANalytical X'Pert PRO MPD diffractometer employing Cu K α radiation from 5 to 80 ° 2 θ in steps of 0.04 ° and a time per step of 1 s⁻¹.

Thermoanalytical measurements were performed on a Mettler Toledo TG/SDTA 851° instrument. During dynamic measurements, the temperature ranged from room temperature up to 900 °C for the xerogels with the heating rate of 5 K/min. Differential scanning calorimetry (DSC) measurements were made with a Mettler Toledo DSC 822° instrument. The baseline was subtracted in all cases. Xerogel intermediates used for Fourier transform infrared (FT-IR) spectroscopy and X-ray diffraction (XRD) analyses were prepared in dynamic TG measurements up to the chosen temperature. Platinum crucibles were used for TG measurements and aluminum crucibles for DSC measurements.

FT-IR spectroscopic measurements were made using a Perkin Elmer System 2000 spectrophotometer with a resolution of 4 cm⁻¹. KBr pellets embedded with xerogels intermediates were prepared for this purpose.

The mass of the deposited TiO₂ was estimated by weighing the substrate before and after the deposition and calcination.

The surface hydrophilicity of thin films on SiO₂-coated soda-lime glass was studied in ambient air at room temperature using a horizontal microscope with a protractor eyepiece. For this purpose, a Contact Angle Meter (CAM-100), KSV Instrument, Ltd. Finland, was used.

Thickness and morphology of the thin films were analysed with Hitachi S 4,700 scanning electron microscope (SEM).

2. 4. Photocatalytic Experiments

Photocatalytic measurements were performed by using a continuous flow reactor. The reactor was purged with oxygen and cooled with tap water, which resulted in a constant reaction temperature of 25 °C. It had on-line capability for measuring UV-Vis spectra of the solution. A 335 nm cut-off filter was used in front of the photocatalytic cell and a 125 W Xe lamp (Cermax xenon parabolic lamp) as a light source. Photocatalytic cell is constructed in such way, that glass substrate represents one of the cell's walls. Thus, one side of titania film was immersed in the solution of azo-dye Plasmocorinth B (40 mg/L). Chemical structure of Plasmocorinth B is presented in an insert in Figure 6. The dye solution was continuously purged with oxygen. A peristaltic pump (Heidolph PD 5001) was used to drive the solution from the reactor to the UV-Vis spectrophotometer for on-line absorbance measurements and back.

3. Results and Discussion

3. 1. Characterization of the Thin Films and Xerogels

Thin films were prepared on soda-lime glass, platinum and aluminum foil (to investigate the adhesion to various substrates), but for the photocatalytic studies thin films on soda-lime glass substrate (mostly SiO₂-coated) were used for the sake of convenience.

Primary sol remained transparent and stable for months kept in refrigerator; no coagulation or precipitate appeared. The pH value of the sol was about 7. Four different samples, based on the P25 loading, were prepared: sample 0 with no addition of P25, sample 5P25 with 5 g/L of P25, sample 10P25 with 10 g/L of P25 and sample 20P25 with 20 g/L of P25 Degussa TiO₂ powder. Films made from P25 loaded sols were semitransparent and uniform. Before the deposition sols were ultrasonicated for 30 minutes to prevent agglomeration of P25. The P25 loaded sols with higher concentration of P25 were unstable, thin films were uniform only if made from freshly prepa-

red sol. Homogeneity of the aged, heavily loaded sol could not be achieved even with ultrasonication for few hours.

3. 1. Thermal Behaviour

TG and DSC curves for the as-dried powder of primary sol (0) are presented in Figure 2a. The first step in the weight loss curve is ascribed to dehydration, which occurred up to 200 °C. The weight loss up to this temperature was 26%. Then the thermal decomposition of titanium peroxide to oxide began, which is evident from the second step (onset temperature ~ 240 °C) of the TG curve. The existence of peroxy groups in thermally untreated xerogel was confirmed by FT-IR measurements. Total weight loss up to 400 °C was 32%.

It is known that a peroxotitanium complex is produced by adding H₂O₂ to TiCl₄ aqueous solution.¹⁶ It is a dinuclear complex of composition Ti₂O₅(OH)_x^{2-x} (x = 1-6) at pH above 1. Above pH 3 (x > 2), the dinuclear complex turns into anions or Ti₂O₅(OH)₂. Units of Ti₂O₅(OH)₂ slowly condense by forming hydroxy bridges between metal atoms, and finally yellow precipitate of peroxotitanium hydrate, (Ti₂O₅(OH)₂)_∞ is obtained. If water is coordinated on each Ti, the formula is Ti₂O₅(OH)₂ · 2H₂O. The theoretical value of weight loss from Ti₂O₅(OH)₂ · 2H₂O to TiO₂ is 35%, which is in accordance with our measurement.

In the DSC curve (Figure 2a) the endothermic peak with its minimum at 80 °C is due to water evaporation. The first broadened exothermic peak originates from decomposition of peroxy groups and the second one, with its maximum at 360 °C is ascribed to crystallization of amorphous phase to anatase.

A comparison of TG curves for thin film on aluminum foil and for the corresponding xerogel is presented in Figure 2b. Aluminum foil was used as a substrate for the films to obtain a low substrate to film mass ratio (S/F). When soda-lime glass is used as a substrate high S/F ratio

results in very small mass changes, which are in the range of buoyancy and aerodynamic effects. Resemblance of the two curves is obvious, where thermal decomposition for both samples occurred up to 350 °C and the onset temperatures are nearly the same. Therefore, xerogel samples were used for XRD measurements.

3. 2. Contact Angle Measurements

The interaction between thin film surface and water was estimated by contact angle measurements. The change of the water contact angle was tested as a function of time during UV illumination (peak value at 355 nm) with UVA radiation of intensity cca. 4 mW/cm² for thin films 0 and 20P25. The results obtained and shown in Table 2 confirm higher hydrophilicity of thin film 20P25. The observed photoinduced hydrophilic property for both thin films indicates their self-cleaning ability.

Table 2. Water contact angles as a function of time during UV illumination.

Time of UV illumination [min]	Contact Angle [°]	
	Thin Film 0	Thin Film 20P25
0	32,6	20,0
10	21,5	6,8
20	12,5	3,5

3. 3. Variation of TiO₂ Mass With Viscosity

The primary sol was diluted with water to get suitable viscosity for the deposition of the films. As expected, the film thickness increased with the increase in viscosity. Optimal films with maximum adhesion were made from sol with the viscosity around 80 cP. The films made from sols with greater viscosity were thicker, but after drying in air at room temperature they got detached or could be peeled off the substrate.

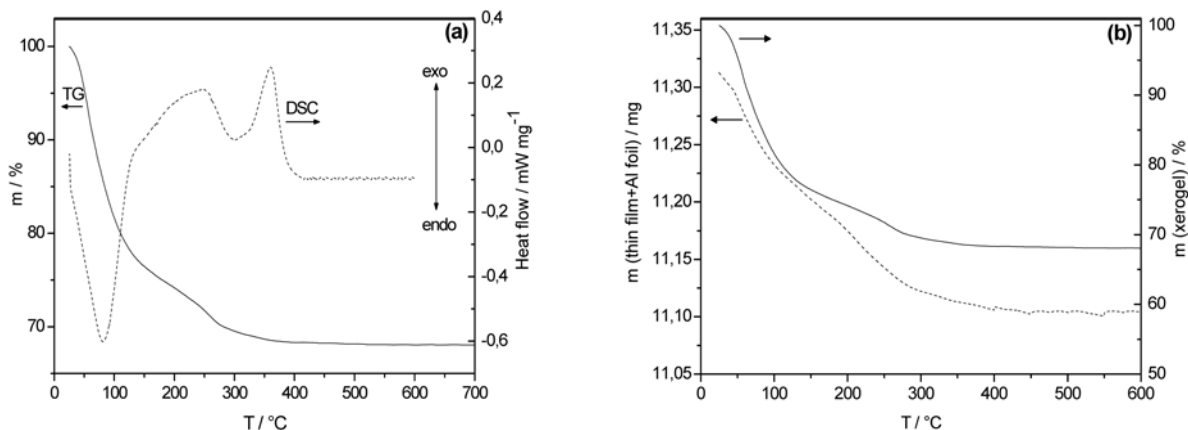


Figure 2. TG and DSC curve for the primary gel dried at room temperature (a) and comparison of TG curves for xerogel and thin film on aluminum foil (b).

Table 3 presents the measured masses, calculated masses of TiO_2 per unit of substrate area and thickness of four layered films deposited on the SiO_2 support. The mass of titania films and thickness of the thin films increased along with the loading of P25 increase.

Table 3. The measured masses, calculated masses of TiO_2 per unit of substrate area and thicknesses for different four-layer films deposited on SiO_2 -coated soda-lime glass substrate.

Thin film sample on SiO_2 support	Titania mass (mg)	TiO_2 mass per unit of substrate area (g/m^2)	Thin film thickness (nm)
0	1,0	0,7	150
5P25	1,2	0,8	150
10P25	1,3	0,9	300
20P25	1,6	1,1	500

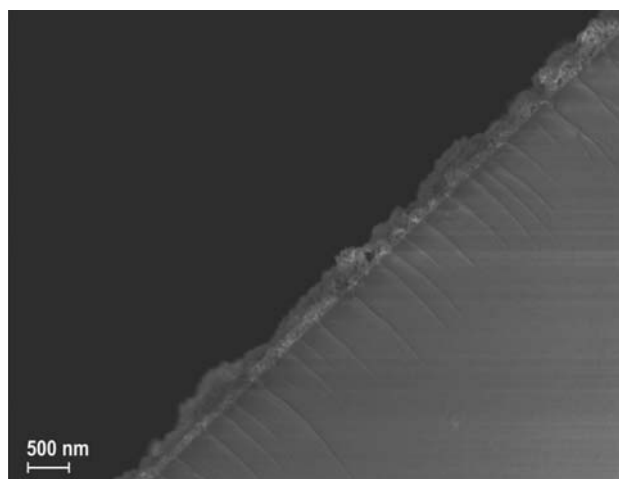


Figure 3. SEM micrograph of the thin film 10P25 deposited on SiO_2 -coated soda-lime glass.

The SEM picture of the thin film 10P25 is presented in Figure 3. It shows that the thin film consist of homogeneously distributed spherical TiO_2 grains. The estimated thin film thickness for sample 10P25 is 300 nm.

3. 4. Crystal Structure

Figure 4 presents the evolution of XRD spectra of the xerogel with increasing temperature. Due to distinctive difference in intensities between lower (25–500 °C) and higher (600–900 °C) heat-treatment temperature the spectra are presented in two graphs.

The untreated xerogel, dried in air at ambient temperature, showed the diffraction profile of an amorphous material, which indicates that TiO_2 films were amorphous in nature. The crystalline phase of samples heat-treated from 350 to 700 °C is predominantly anatase, whereas the sample treated at 800 °C shows some weak peak characteristic for the rutile phase. This indicates that the anatase phase is stable up to 700 °C and rutile phase starts to grow above this temperature. The crystalline phase of the sample treated at 900 °C is a phase mixture of anatase and rutile.

The particle size of xerogels heat-treated at 500 °C and 600 °C were calculated by Scherrer formula:

$$D = \frac{k \cdot \lambda}{\beta \cdot \cos \theta} \quad (1)$$

Where k is Scherrer constant, λ indicates the wavelength of the X-ray (0,154178 nm), β is the full width at half maximum of the peak and θ is the position of the peak.

The estimated size of crystallites by using the above formula is about 13 nm (500 °C) and 36 nm (600 °C).

The size of particles increased with the temperature. To ensure small particle size, considering that the anatase

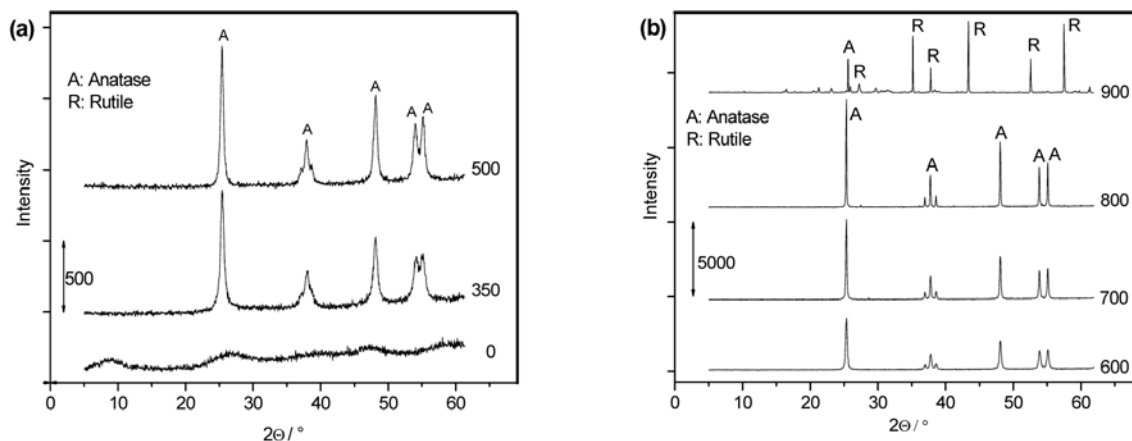


Figure 4. XRD pattern of untreated xerogel, xerogels heat treated at 350 °C and 500 °C (a) and XRD patterns of xerogels treated at 600, 700, 800 and 900 °C (b).

phase is more active, and that soda-lime glass was used as a substrate, we chose 500 °C as an appropriate heating temperature to prepare the TiO₂ thin films as photocatalysts. Thin films calcined at 350 °C for 30 minutes were less photocatalytically active, which indicates that crystallization from amorphous to anatase phase had not been completed yet. Consequently, the portion of anatase in the mixture was not high enough to perform effective photocatalytic reaction.

3. 5. Light Absorption Properties

Light absorption properties of titania films not only depend on the films themselves, but also on the substrate.¹⁵ Therefore a comparison of light absorption of thin films on different substrates was made. For the same reason the influence of the substrate on photocatalytic activity was examined (see section 2.). The influence of soda-lime glass and SiO₂ support on UV absorption characteristics was examined for thin films made from sols 0 and 10P25 and is presented in Figure 5.

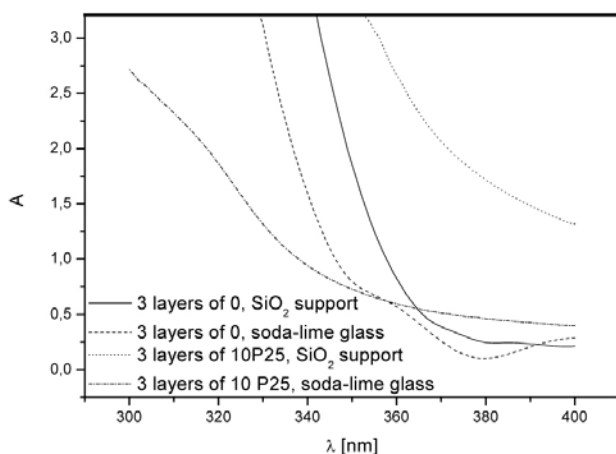


Figure 5. Comparison of UV absorption for thin films 0 and 10P25 on soda-lime glass and SiO₂ support.

Films, deposited on soda-lime glass, absorb much less light between 300 and 400 nm than the same films deposited on SiO₂-coated soda-lime glass substrate. The most striking difference was observed in the UV light absorption of the thin film deposited on different supports made from P25 loaded sol. This extensive UV light absorption is reflected in photocatalytic activity of thin films made from sols with P25 loadings.

3. 6. Photocatalytic Properties

The photocatalytic activity of the thin film catalysts was determined by photocatalytic decolorisation of azo-dye Plasmocorinth B. Figure 6 represents

UV–Vis spectrum of Plasmocorinth B between 200 and 1000 nm. Chemical structure of this azo-dye is presented in the insert.

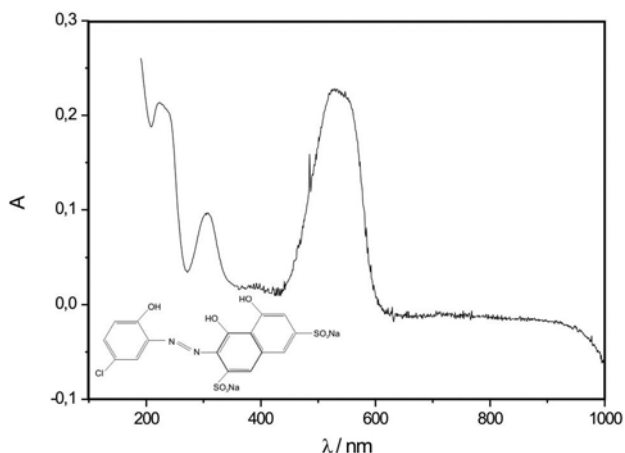


Figure 6. UV–Vis absorbance spectrum of Plasmocorinth B aqueous solution with concentration of 40 mg/L.

Photodecolorisation of Plasmocorinth B by thin film from primary sol on a soda-lime glass was slower than that of a thin film on SiO₂ support as shown in Figure 7. It has been reported that sodium cations diffuse into the titania layer during heat treatment which results in lower UV light absorption (Figure 5) and consequently also in lower photocatalytic activity.^{15, 17}

H.-J. Nam et al. report that Na⁺ in the TiO₂ sol-gel film increases the amorphous – anatase phase transition temperature and that Na⁺ in the film affects the photocatalytic activity of the TiO₂ films through changing the particle size of anatase in terms of the carrier separation process in the primary particles.¹⁸

Our photodegradation studies show that photocatalytic activity of the films grows with the increase in con-

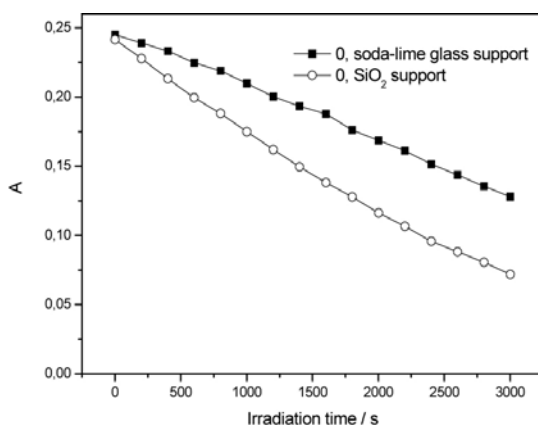


Figure 7. The influence of substrate (soda-lime glass and SiO₂ support) on photodecolorisation of Plasmocorinth B in contact with thin films 0 (4 layers).

centration of P25. All thin films for this photocatalytic experiment were deposited on soda-lime glass with a protecting SiO₂ layer. Figure 8 shows photobleaching curves – absorbance at 526 nm as a function of irradiation time – of the dye solution in contact with various titania films. The most striking difference was found when comparing the thin film 0, deposited from primary sol and thin film deposited from sol with highest P25 loading (20 g/L, thin film 20P25). The addition of 20 g/L of P25 promotes the photodegradation rate constant which is 6.5-times higher.

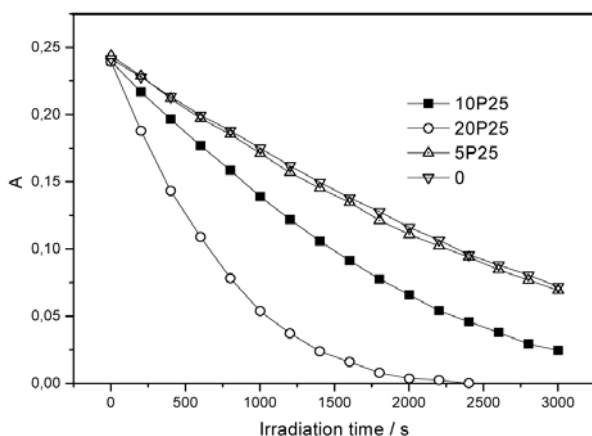


Figure 8. The impact of P25 concentration in the primary sol on photodecolorisation of Plasmocorinth B in contact with different thin films (4 layers on SiO₂ support).

Degradation of aqueous Plasmocorinth B indicates first-order kinetics, therefore all degradation curves were fitted as first-order reactions. The calculated mean half-lives are presented in Table 4.

Table 4. The calculated half-lives and rate constants for photodecolorisation of aqueous Plasmocorinth B.

Thin film sample	Half-life (min)	Rate constant (min ⁻¹ × 10 ⁻³)
0	28.8	24.0
5P25	28.8	24.0
10P25	14.4	48.0
20P25	4.44	156

There is no change in the rate constant at small amounts of added P25 (under 5 g/L) to Ti-peroxo sol. SEM micrographs showed, that the thickness for both samples is 150 nm. The rate constants of thin films' photocatalytic activity increase linearly with the mass of P25 loading when the concentration of added P25 is higher than 5 g/L. The half-life for the degradation reaction of Plasmocorinth B is 6.5-times smaller in case of 20P25 thin film than in case of thin film deposited from primary sol (0). All the thin films compared consisted of four la-

yers, but the masses of TiO₂ per unit of substrate area and also thickness of the thin films increased with loadings of P25 (Table 3). However, the enhancement of photocatalytic activity was not only due to the increase of TiO₂ mass. The mass ratio between thin film 20P25 and 0 is 1.6, while the rate constant for photodecolorisation of the sample 20P25 is 6.5-times higher than in the case of sample 0, as stated above. Increase in photocatalytic activity could be also ascribed to film thickness, since it has been reported, that film thickness has a marked influence on photocatalytic activity, showing a strong increase up to 300–400 nm, followed by a much shallower slope.¹⁹

4. Conclusions

Alkaline sols for dip-coating deposition of thin films were made from TiCl₄/EtOH aqueous solution. Alkalinity of the sols enabled the implementation of metals as a substrate in the system. Our results showed that adding Degussa P25 powder to Ti-peroxo sol considerably increases photocatalytic activity of thin films and improves adhesion to the substrate which we also observed. The rate constants of photodecolorisation increase linearly with the concentration of P25 in the sol. To ensure small anatase particle size and considering that soda-lime glass was used as a substrate for photocatalytic studies, 500 °C was chosen as an appropriate heating temperature to prepare the TiO₂ thin films as photocatalysts.

Thin films made from modified Ti-peroxo sols exhibited higher hydrophilicity, which can eventually contribute to better self cleaning ability. The results reveal that the substrate plays a crucial role in UV light absorption properties and photocatalytic activity.

The comparison of TG curves for xerogel and thin film on aluminum foil showed nearly the same course of thermal decomposition. Thermal analysis confirmed the structure of peroxotitanium dinuclear complex.

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Povzetek

Optično polprepustne tanke plasti TiO_2 smo pripravili po sol-gel postopku iz prekurzorja TiCl_4 in dodatkom različnih koncentracij komercialnega TiO_2 Degussa P25. Tanke plasti smo s tehniko potapljanja nanegli na različne podlage, posušili na zraku, jih 30 minut žgali pri $500\text{ }^\circ\text{C}$ in tako dobili plasti z dobro oprijemljivostjo. Uporabili smo različne podlage: natrijevo steklo prevlečeno z zaporno SiO_2 plastjo, platinsko in aluminijevo folijo. Tanke plasti in prahove pripravljene iz solov smo analizirali s termogravimetrijo, DSC analizo, rentgensko difrakcijo, UV–Vis spektroskopijo, SEM mikroskopijo, FT–IR spektroskopijo in z merjenjem kontaktnih kotov.

Dodatek P25 v primarni sol znatno pospeši fotokatalitsko razgradnjo vodne raztopine azo barvila Plazmokorinta B, kar smo spremljali z *in-situ* UV–Vis spektroskopijo.