

## METHODS FOR PREPARATION AND CHARACTERISATION OF SELF-CLEANING SURFACES

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Recently, environmental purification using photocatalysts has been an active area of investigation. Titanium dioxide ( $\text{TiO}_2$ ) is recognized to be appropriate material for photocatalyst because of its strong oxidizing power under UV irradiation. There are several other compounds which have the ability to catalyze under UV light, such as Cadmium Sulfate, but unlike Titania, they are highly toxic. Titanium dioxide naturally occurs in three different crystal structures; their band gap is slightly different. Two modifications anatase and rutile are of significant industrial importance. It is proven, that anatase is by far more photo-active modification of titanium dioxide compared to rutile. In our research a procedure for preparation of self-cleaning textile surfaces was studied, i.e. a composite of  $\text{TiO}_2$  nanoparticles with silica was used for nanocoating preparation. Photocatalytic activity of untreated and modified fibre was evaluated by determination of the photodegradation oxidation of organic dye under UV irradiation conditions and the coatings morphology was studied on SEM images of fibres surfaces.

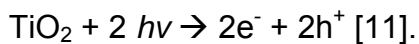
***Key words: Nanocoating, Self-cleaning,  $\text{TiO}_2$ ,  $\text{TiO}_2$  - $\text{SiO}_2$  composite, Textile surfaces, SEM***

## 1. Introduction

Transparent films and coatings of titanium dioxide have been studied for a number of years now [1]. Technological interest has focused around their potential in self-cleaning applications due to their photocatalytic [2, 3] and hydrophilic properties.

Titanium dioxide exists in three modifications with different crystalline structures and therefore altering physical properties. Only rutile and anatase are commercially important. Titanium dioxide is a photoconductor both in anatase and rutile modification. Even though anatase is the most active form of titania [4, 5, 6, 7, 8, 9, 10], some researchers have suggested that a mixture of rutile and anatase is the best combination [4]. Rutile and anatase have different band gaps. The band gap is the energy difference between the valence band and the conduction band in a semiconductor and is the major determinant of the absorption behavior. For rutile this band gap is 3.05 eV, corresponding to absorption at 420 nm. Anatase on the other hand has a band gap of 3.20 eV and absorbs at 385 nm. It was found that the rutile contained in the crystal mixture initially functions as an antenna. This conducts absorbed quanta to the anatase system, thus increasing the probability of generating reactive electrons at the surface. In brief, the coupling of the two absorption processes results in improved utilization of the incident light. An example of such mixture of two polymorph crystalline structures is AEROXIDE® TiO<sub>2</sub> P 25 (Degussa, Germany), which consists of 80 percent anatase and only 20 percent rutile.

When penetrable photon energy is applied, the electron in the Titania valence band will be excited causing the electron to escape resulting in a positive 'hole'. This radical electron has a very high oxidizing energy and it is able to breakdown inorganic and organic chemical bonds. The excitation of Titania by light can be described as:



Much work has been carried out depositing TiO<sub>2</sub> on heat resistant surfaces like glass, ceramics and silica by sol-gel methods. By applying the procedure to the textile surfaces some hindrances appear, i.e. high temperature treatment conditions, fibre damage risks, problems connected with durability of the modification, etc. However some reports of TiO<sub>2</sub> application on fibres can be found [12, 13, 14, 15, 16, 17, 18, 19].

The present presentation deals with TiO<sub>2</sub>-SiO<sub>2</sub> nanocoating preparation and analysis of the coated fibres properties.

## 2. Experimental

### Materials

The following chemicals were used as received: Tetraethyl orthosilicate (TEOS), 98% (Aldrich, Germany), Ethanol, 96% (Riedel-de Haën, Germany), ammonia solution, 25% (Merck, Germany), TiO<sub>2</sub> P25 (Degussa, Germany). Deionised water was used in the preparation of all water solutions.

#### *Lyocell fibres and fabric*

In this research Lyocell materials were used for the deposition of TiO<sub>2</sub> P25 nanoparticles. In the present research Lyocell fibres 1.3 dtex (Lenzing, Austria) and fabric in 2/1 twill weave with S twill line were used.

### Coating methods

Nanocoatings were prepared using two procedures.

In Method 1, before treatment, 5 g/L TiO<sub>2</sub> P25 nanoparticles were pre-dispersed in deionised water, using ultrasound stirring in the Elma ultrasonic cleaning bath with the frequency of 35 kHz at T=60°C for 60 minutes. In addition, TEOS as a precursor in the presence of ethanol as a solvent, 0.5 mol/L ammonia solution as a catalyst entered a reaction. Deionised water as hydrolysis agent was already present in TiO<sub>2</sub> solution. After addition of all the chemicals and approximately 0.2 g of Lyocell sample, ultrasound stirring at 60°C for one hour followed.

In Method 2, gel made of 0.5 mol/L TEOS as a precursor in the presence of ethanol as a solvent, 0.5 mol/L ammonia solution as a catalyst and deionised water as hydrolysis agent was already formed, before TiO<sub>2</sub> P25 nanoparticles entered the process. Silica gel and TiO<sub>2</sub> P25 nanoparticles were stirred for 15 minutes, after that approximately 0.2 g Lyocell sample was added. Ultrasound stirring at 60°C for one hour followed.

After the treatment, samples were rinsed with deionised water and dried at room temperature (T=20±2°C) during the night and heat treated at T=110°C for 15 minutes. In addition, unattached particles of TiO<sub>2</sub> were removed during the 5-minutes lasting ultrasound after-treatment.

### Characterisation

#### *Electron microscopy*

Particles morphologies and coatings properties were studied by transmission Philips CM20 (TEM, ZEISS EM902, Germany) and scanning (SEM, ZEISS Gemini Supra 35 VP) electron microscopy. TEM samples were prepared by drying drops of diluted polymerized emulsions on Cu-grids coated with Formvar films, whereas for SEM samples, the samples were fixed by adhesive carbon band on brass holders.

#### *Determination of modification efficiency – self-cleaning test*

A self-cleaning test was performed on Lyocell fabric. The photo-catalytic properties of coatings were investigated by determination of the photo-degradation oxidation of the

organic dye, after UV irradiation conditions. Untreated and treated samples were soiled by a drop of red beet sap and UV irradiated (exposed to the daylight) for different periods of time at room temperature and the intensity of the decolouration process of the dye applied to the fabric surface was followed by a change in the colour of stain. Datacolor international MICROFLASH 200d apparatus was used for colorimetric measurements.

### 3. Results and discussion

In the Method 1, during the process of gelation, colloid particles of alkoxide (TEOS) form siloxane bonds and a network, which captures  $\text{TiO}_2$  P25 nanoparticles, is formed (Fig.1). In that way silica gel is used as a binder. In the gelation reactions, sol particles were linked in aggregates, which were finally cross-linked in reaction of polymerization to form a solid gel.

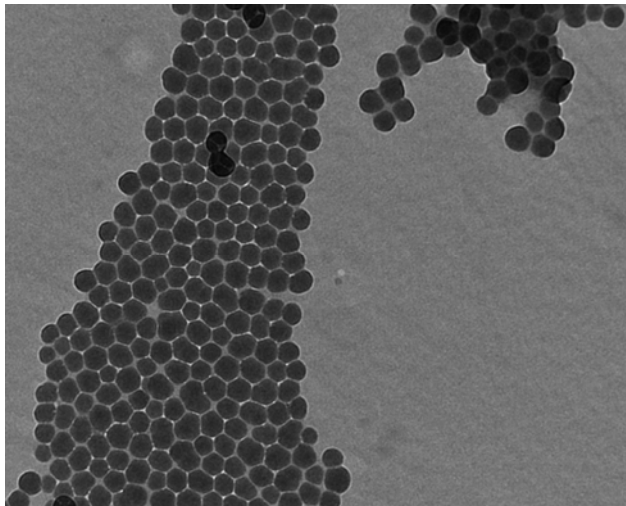


Fig.1. TEM image of a silica network formed by Method 1

Using Method 1,  $\text{TiO}_2$  P25 was readily trapped onto Lyocell fibres by a sol-gel reaction of precursor TEOS. The complex was physically retained in a silica gel coating which is formed on the fibres. A surface morphology of the  $\text{TiO}_2$ - $\text{SiO}_2$  composite nanocoating on Lyocell fibres is shown in Fig.2.

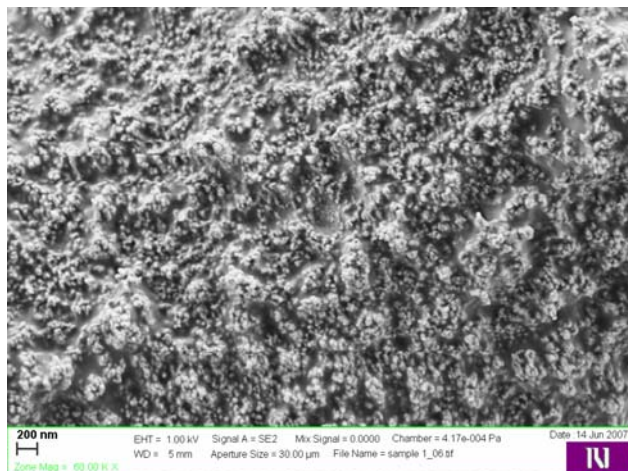


Fig.2. SEM image of TiO<sub>2</sub>/SiO<sub>2</sub> nanocomposite coating obtained by Method 1

In the Method 2, gel was already formed before TiO<sub>2</sub> nanoparticles entered the process. Silica gel and TiO<sub>2</sub> nanoparticles were left to react for 15 minutes. In that time TiO<sub>2</sub> nanoparticles were absorbed on SiO<sub>2</sub> (Fig.3), then Lyocell fibres were added. Due to the reaction of silica surface hydroxyl groups with TiO<sub>2</sub> the adsorption of the coating on fibres surface was prevented.

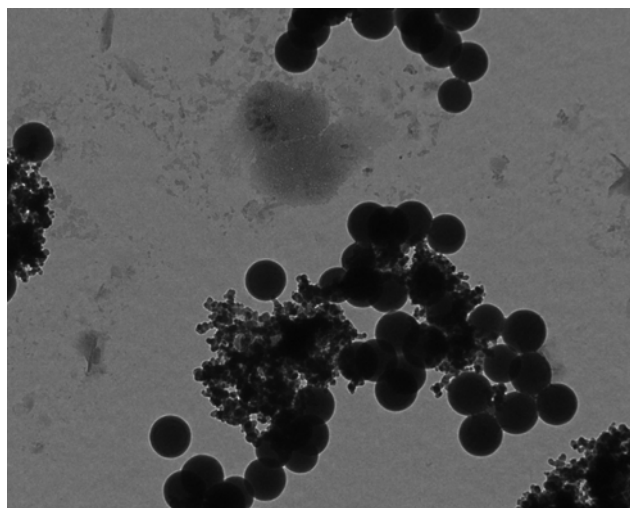


Fig.3. TEM image of TiO<sub>2</sub> P25 particles deposited on the SiO<sub>2</sub> particles (Method 2)

Fig.4 demonstrates surface characteristics of Lyocell fibres treated by the Method 2. A smooth fibre surface can be observed. It indicates that the coating was not formed.

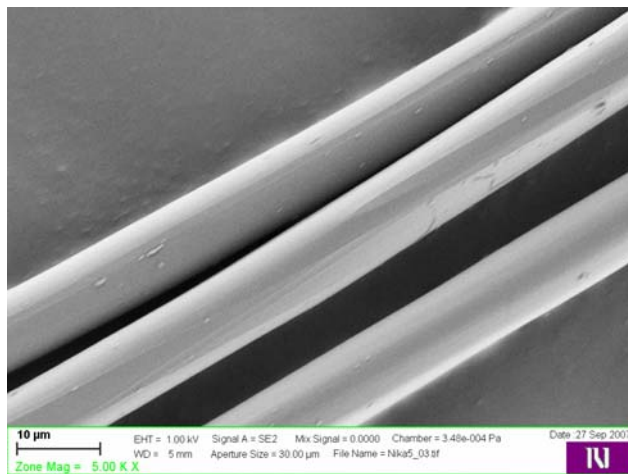


Fig.4. SEM image of Lyocell fibre after the treatment by Method 2

### *Self-cleaning test*

Fig.5 shows untreated Lyocell fabric and Lyocell fabric modified by the Method 1. Both samples were stained and afterward exposed to daylight irradiation. The result of 32 days of exposure to UV irradiation and showering are demonstrated on the Fig.5. The difference between the two samples is evident. The stain on the untreated sample remained almost unchanged, while the stain on the treated sample (Method 1) faded and nearly disappeared.

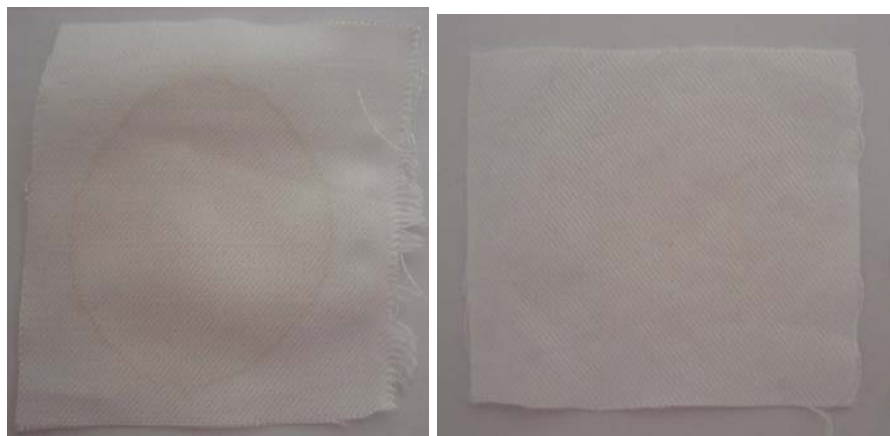


Fig.5. Untreated and modified Lyocell samples after self-cleaning test

The results of visual determination were confirmed by colorimetric measurements. For that reason the chroma ( $C^*$  component) of CIELAB system was investigated. From the results obtained by self-cleaning test we can conclude that coating obtained by Method 1 is effective. The longer treated fabric was exposed to the daylight the lower was the value  $C^*$  of the stain. That means that in the beginning the colour of the stain was expressive and become less-expressive with time. Significant changes in  $C^*$  of the stain happened in 8 days after the beginning of the test. For the comparison we performed parallel test on untreated Lyocell sample. The change in  $C^*$  was insignificant. Similar

results were obtained for the sample treated by Method 2. The results are demonstrated in Fig. 6.

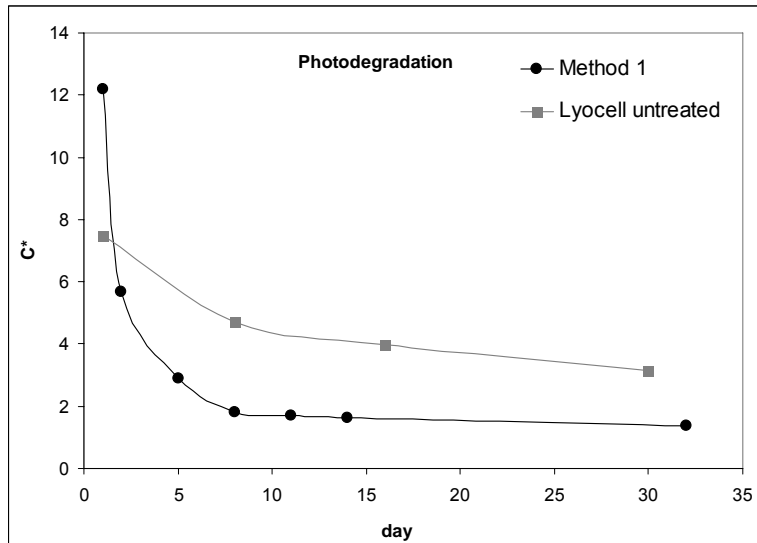


Fig.6. Photodegradation as a function of time

An illustration of the stain colour changes is presented by the change of  $L^*$  (lightness component) of CIELAB system as well (see Fig.7). The lightness ( $L^*$  component) of the irradiated stain on Lyocell fabric ( $L=87.69$ ) modified by Method 1 approached to the  $L^*$  of the modified Lyocell fabric before the staining ( $L=89.44$ ). In the meantime the  $L^*$  of the stain on the untreated sample changed negligible. The results obtained for Method 2 were the same as results obtained for untreated sample. The results obtained by determination of component  $L^*$  confirm the results of the component  $C^*$  determination. We can conclude that by applying Method 1 on fibres surfaces we succeeded in achieving nanocoatings with self-cleaning properties.

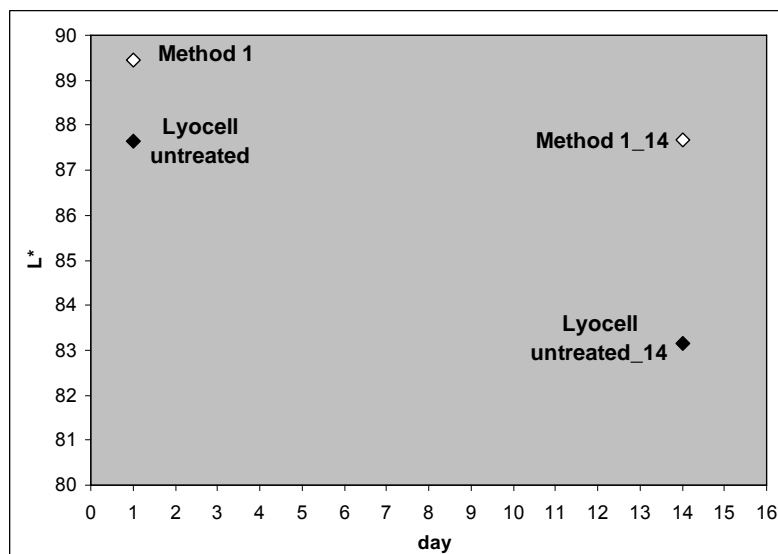


Fig.7. The lightness ( $L^*$  component) of CIELAB system was investigated

#### **4. Conclusion**

Two procedures for preparing  $\text{TiO}_2\text{-SiO}_2$  composite nanocoatings on the surface of regenerated cellulose fibres were used. Homogeneous coatings with excellent photocatalytic activity originated using Method 1, since  $\text{TiO}_2$  nanoparticles efficiently attached on the surface of Lyocell fibres, while Method 2 did not form an efficient coating.

Future work will be focused on study the optimization of the nanocoating process and on determination of the precise structure of nanocoatings.



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