



norden

Nordic Innovation Centre

March 2009

FUNCOAT - Enhanced functionality of selfcleaning and antibacterial surface coatings

- A brand new product for a small company working with flat glazed surfaces
- Achieving a smooth thin coating with a functional performance
- Hydrophobic surfaces with UV-illumination



Authors: Jyrki Mäkelä and Mikko Aromaa

Participants

Research institutes:

1. Tampere University of Technology/ Aerosol Physics Laboratory (TUT), Finland
2. Åbo Akademi – Process Chemistry Centre (ÅA), Finland
3. Lund University / Faculty of Engineering - Nanocrystals Group (LTH), Sweden
4. Glasforskningsinstitutet (GLAFO), Sweden
5. Technological Institute of Iceland (IceTec) , Iceland

Companies:

6. Beneq Oy, Finland
7. IDO Bathroom Ltd, Finland

Subcontractors for TUT:

8. University of Helsinki /Laboratory Inorganic Chemistry (LIC), Finland
9. University of Helsinki/ Microbiology (MB), Finland
10. Micronova/ Helsinki University of Technology (HUT)
11. Crystal Fibre (CF), Denmark

Title: FUNCOAT - Enhanced functionality of self-cleaning and antibacterial surface coatings		
Nordic Innovation Centre project number: 06120		
Authors: Jyrki Mäkelä (Doc), Mikko Aromaa (M.Sc.)		
Institution(s): Tampere University of Technology		
Abstract:		
<p>The goal of the project was to coat ceramic tiles with titanium oxide- silver nanoparticles, to achieve a smooth thin coating with a functional performance, with both photocatalytic and antibacterial properties. A fine quality multicomponent nanocoating was fabricated on the tiles, and a vast amount of scientific analysis of the nanoparticles from the process and of the particles on the coating were performed. The surfaces were hydrophobic, and became hydrophilic with UV-illumination. The coatings were photocatalytic, but the obtained photocatalytic reaction rate coefficients were smaller than originally expected. Also, biofilm removal was achieved but remained lower than expected. The lower efficiencies were due to thinness of the coating, i.e. the small amount of material on the surface. The surfaces were functional, but for commercial breakthrough, increasing the thickness of the film without losing the transparency requires research and development.</p>		
Topic/NICE Focus Area: <u>Micro- and NanoTechnology (MINT)</u>		
ISSN:	Language: English	Pages: 21
Key words:		
Distributed by:		
Contact person:		
<p>Jyrki M. Mäkelä, Doc. Lecturer Tampere University of Technology, Department of Physics, Aerosol Physics Lab. P.O.Box 692, FIN-33101, Tampere Finland E-mail: jyrki.makela@tut.fi Tel: +358 3 3115 2532 Mobile: +358 40 733 5405 Fax: +358 3 3115 2600</p>		

Executive summary

The purpose of the project was:

- Develop further an existing coating process for ceramic tiles
- Achieve new functional properties for the ceramic tiles
- Survey commercialization of the method

The study has achieved this aim by:

- Improving the functionality of the tiles
- Finding a process window for the technique
- Giving suggestion of how to achieve commercialization in future

Method

In this project, a variety of ceramic tiles were coated with titanium oxide-silver nanoparticles. The goal was to achieve a smooth thin coating with a functional performance, with both photocatalytic and antibacterial properties. A fine quality multicomponent nanocoating was fabricated on the tiles, and a vast amount of scientific analysis of the nanoparticles from the process and of the particles on the coating were performed. State-of-art analysis were used both on characterizing the surfaces and testing the opacity and functionality of the coatings. Also a novel technique was developed for determination of the depth profile of the coating.

The practical objectives for the project have been:

- **Optimising the process parameters** for a single-step flame based process, where silver (Ag) and titanium oxide (TiO₂) binary nanoparticles are generated and deposited on a glass or tile surface.
- **Designing the process equipment** for industrial production
- **Testing the end products**
- **End user feedback**

Main results from the quantitative study:

- Titania – silver nanocomposite coatings were successfully produced in an industrial scale on commercial ceramic tiles and float glass
- Coatings were optimized so that the surface coverage was 100 %
- Coatings are composed of titania nanoparticles of 10-20 nm and silver nanoparticles of 1-3 nm (1 wt-% of titania) which are attached on the surface of titania spheres and are also separately in the coating
- The crystal form of titania includes both anatase and rutile and the crystal phase is not size dependent
- Method of analyzing the depth profile of the coating was developed
- Verification of the functionality of the fabricated thin coatings turned out to be challenging. The coated surfaces were hydrophobic, and became hydrophilic with UV-illumination. The coatings were photocatalytic, but the obtained photocatalytic reaction rate coefficients were smaller than originally expected. Also, it turned out that standard testing procedures for the capability of the prepared surfaces for biofilm removal, do not presently exist for thin films. The obtained biofilm removal rates were low.
- The coatings were capable of decomposing methylene blue, although the decomposition rates were relatively low. However this was expected from the previous work with stainless surfaces
- Water contact angle was increased on the coated surfaces and UV-light decreases the contact angle
- The core partners of the project still continue co-operation. Of the material of the project, one M.Sc. Thesis, One Ph.D. thesis, and preparation for two other Ph.D.-theses were accomplished during the project.

The following conclusions can be drawn from the results of the study:

- The surfaces fabricated were functional, but the effect was too small for an accomplished industrial product.
- Optimization of multi-functionality and transparency will be challenging
- Development of functional coatings is an on-going branch of R&D in this area of nanotechnology. Since improvement for the functionality was achieved and a clear process window was determined, this project will help similar development in the future.

Recommendations for continued studies:

- Coating thickness needs to be increased to achieve strength of functionality
- For commercial breakthrough, the amount of the nanomaterial ($\text{TiO}_2 + \text{Ag}$) on the surface needs to be increased, but still, the coating must be transparent.
- This topic, i.e. how to maintain the transparency of the coating, still requires research and development.

Contents

Participants	ii
Executive summary.....	iv
Contents.....	1
Introduction	2
Background.....	3
Development.....	4
Matrix for the experiments	5
Analysis.....	6
Nanoparticles from flame	6
Structure of coatings.....	9
Performance of the Product	14
Miscellaneous	18
Contribution of partners.....	18
Company contribution:	18
Publication activities	19
Summary	20
References	21

Introduction

Products with self-cleaning and/or antibacterial surfaces include self-cleaning windows hydrophilic ceramic tiles and antibacterial refrigerators. Processes for generating titanium dioxide based photocatalytic surfaces and silver based antibacterial surfaces are known. Finnish company Beneq Oy (merged with former ABR Innova Oy) provides technology and equipment for production of self-cleaning surfaces, namely technique labeled nHALO. Their customers show growing interest on improved technology for producing such surfaces, here a flame-based nanoparticle deposition process, commonly

In the Liquid Flame Spray (LFS) method, the precursor liquid is sprayed into the H_2-O_2 flame. Compared to other methods for nanoparticle generation, the cost efficiency of flame processes is relatively high. The LFS was first used in the colouring of glass surfaces. The additional heat from the flame is useful in the glass surface processing. Experimental results on the LFS characteristics have been shown producing Al_2O_3 , metal particles such as silver, palladium and iron oxide and also silica and Ag-Pd alloy particles. Also ceramic titania nanoparticles for coating applications were produced recently. In the most recent article (Keskinen et al. 2006), silver-titania composite particle generation has been studied and its potential for hybrid surface fabrication has been discussed. This recent research at Tampere University of Technology (Keskinen et.al. 2004, Mäkelä et. al. 2006) has lead to a flame-based process for production of surfaces where self-cleaning photocatalytic and antibacterial properties are combined, and can be manufactured in a single-step process (Keskinen et al. 2006). The results show that the functionality of such coatings is outstanding. However, in order to successfully commercialize this process, in-depth co-operation between nanoparticle generation, industrial coating development and end-product quality specification is required.

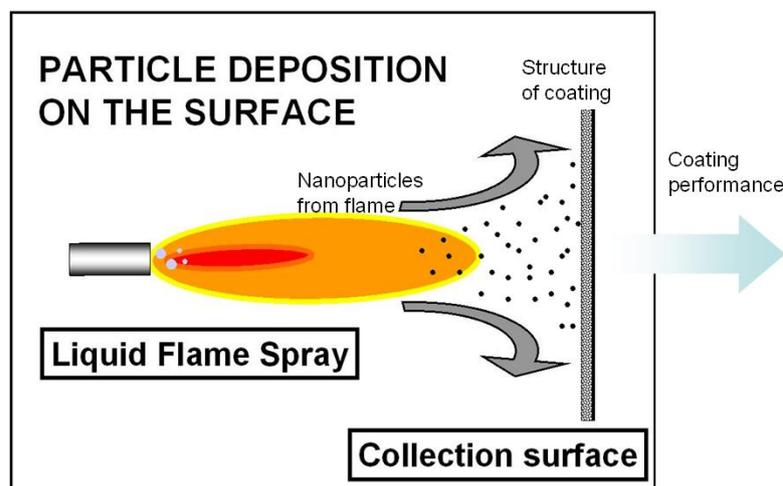


Figure 1. A schematic of applying Liquid Flame Spray process for particle deposition on surface.

Background

In the FUNCOAT project, the goal was to do research in order to commercialise an industrial coating process for glass and glazed surfaces. For this we studied the operational parameters to find an optimal process window. From the previous studies, we know that when using a Liquid Flame Spray (LFS) method with titania and silver precursors, we can generate a surface coating with both photocatalytic and antibacterial properties (Keskinen et al., 2007). Those previous results show that the functionality of such coatings is good. However, in order to successfully commercialise this process, in-depth co-operation between nanoparticle generation, industrial coating development and end-product quality specification was required.

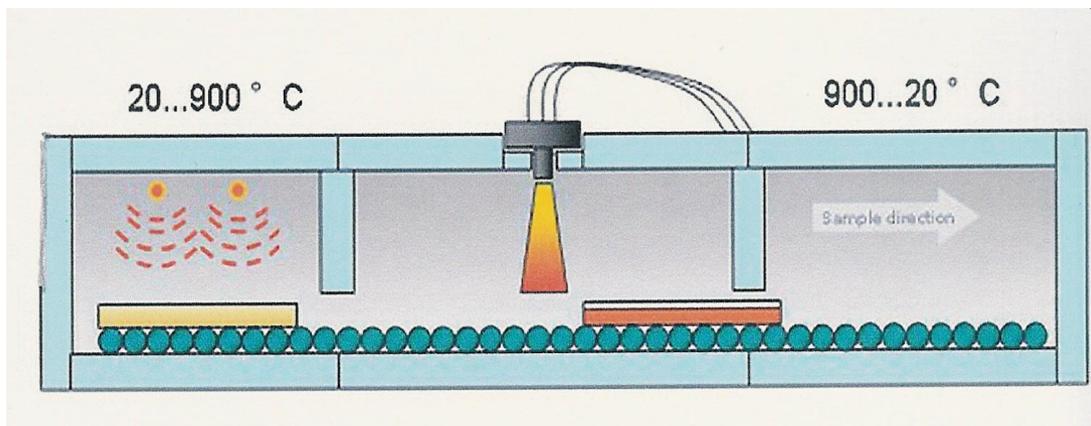


Figure 2. Schematic of the process. From left: heating zone, flame zone, cooling zone. (Taken from homepage of Beneq Ltd)

As is shown in Figure 2., the industrial coating process contains pre-heating of the substrates to be coated, flame processing by LFS/nHALO, and finally cooling down of the hot tiles. In the first part of the work, we searched for optimal temperature of the substrates and optimal flame processing parameters for the technique.

Development

TUT/Aerosol has already previous knowledge of TiO_2/Ag anti-microbial surfaces. The knowledge was used in order to obtain the property on a totally different material, ceramic tile. Ceramic tiles differ from stainless steel surfaces in many ways. The most important difference is that the coating process needs to be made in an oven in order to avoid tensions in ceramic tiles and glazings. The heat-up and cool-down process is the key for producing tiles of good quality. Also the surface of the tiles is much different from stainless steel. Tiles are glazed. The glazing is molten during the coating process. Therefore, nanoparticles go inside the surface as well. Dissolving silver in the glazing needs to be avoided, because silver produces yellowish colour in the glass.

The development of the product started from searching the optimal processing window for the coatings. We studied several different parameters including coating temperature, burner distance, precursor mass flow and concentration. Coatings were applied on different substrates. We chose commercial sanitary ceramics from IDO Bathroom and research sanitary tile from Åbo Akademi as substrates for the study. Several samples were prepared and water contact angle test was chosen to be the standard method for choosing the best parameters in the chase for parameter window. Hypothesis was that hydrophilic surfaces are the ones that have the best performance. Therefore, water contact angle estimation by bare eye was a quick and cost efficient way to browse through the many different samples. The best performing parameters were chosen for future studies. Also, yellow colour due to silver was avoided in the best performing tiles.

The substrates were coated with $\text{TiO}_2\text{-Ag}$ nanoparticles using LFS/nHALO. After processing and cooling, the samples have been wiped/cleaned systematically with cloth and isopropanol to remove the excess nanoparticles from the surface. All the surfaces were analysed using various tests in order to investigate the coating morphology and performance.

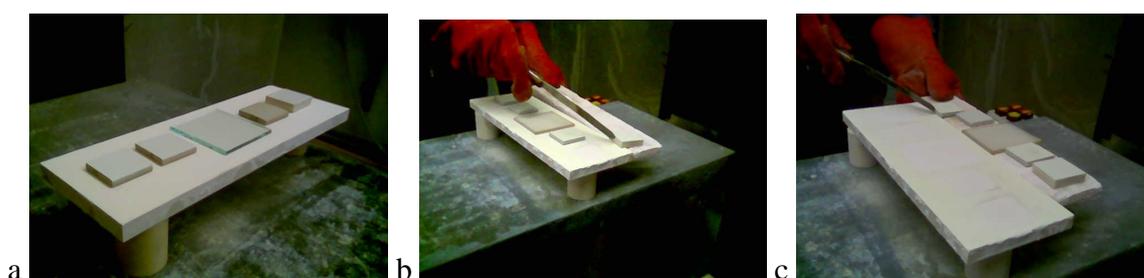


Figure 3 a, b, c. The tray on which the sample substrates are transported through the flame. Figs b & c. The coated samples are moved from the tray into the cooling furnace.



Figure 4 The cooling furnace with some samples in it. (Beneq Oy)

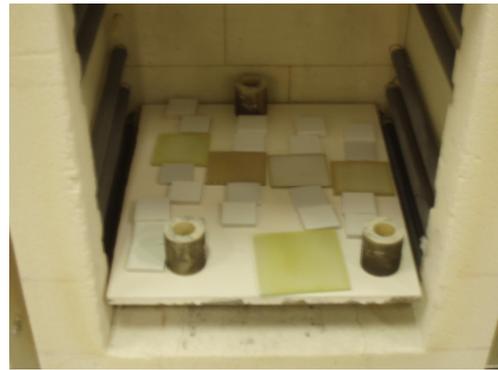


Figure 5. Samples in water contact angle test. (Beneq Oy)

Matrix for the experiments

In the beginning part of the project, a large variety of different process parameters was surveyed. On the original measurement matrix, several values and their combinations were included

- 1) Process temperatures: 500, 550, 600, 650 °C
This is the temperature of the substrate (measured by pyrometer) before entering into the flame. Note, that the flame also heats up the sample.
- 2) Liquid precursor feed rate, 5 - 10 ml/min;
precursor concentration to fulfil production rates of 50 & 25 mg/min for TiO₂, plus Ag in 1wt % of TiO₂.
- 3) Gas flows of O₂/H₂/N₂ in the order of 20/40/15 l/min.
- 4) Distance between torch head and substrate varied between 130-170 mm
- 5) Substrates
Float glass (F) (presently as a test reference),
Ceramic tiles: Pukkila Glossy (K), Pukkila Matt (M),
IDO Glossy (IDO), ÅA Matt (3A)

Later on in the project the matrix was compressed into a concise set, shown in Table 1. Also, the number of surfaces were decreased to 3: Float glass (F) reference, IDO Glossy (IDO) and ÅA Matt (3A).

Table 1. Settings for the 4 core samples of the project.

Process temperature \ Distance from burner	130 mm	170 mm
500 °C	Sample 3	Sample 2
600 °C	Sample 4	Sample 1

All the samples were later on prepared along with this set.

Analysis

Nanoparticles from flame

In the actual coating process with LFS/nHALO, the nanoparticles are first formed in the gas phase and then deposited onto the surface (e.g. Mäkelä et al 2006). Therefore we have a possibility to sample the nanoparticles from the flame using a specially designed collector (Aromaa et al. 2007).

TEM analysis showed that the particulate matter generated by the liquid flame spray consists of TiO_2 nanoparticles of around 10-20 nm (Fig. 6). According to the selected area electron diffraction (SAED), the titanium dioxide is crystalline and consists of both anatase and rutile. In the samples, also smaller silver particles of 1-3 nm were found, which lie on top of the titania particles (Fig 7-9). Also separate Ag nanoparticles ($d_p = 1-3$ nm) were found on the carbon film. This means that the silver is not only on top of titania. Thirdly, as is known from the general analysis of the flame spray techniques, also somewhat larger titania particles, residual particles can be found in the flame. These particles are known to remain when each primary spray droplet is evaporated but a small core particle remains, with size around 50 – 200 nm (Fig 12).

It is known, that the nanoparticle size can be controlled varying the mass flow rate of the precursors (Mäkelä et al. 2004), which again relates to particle production rate.

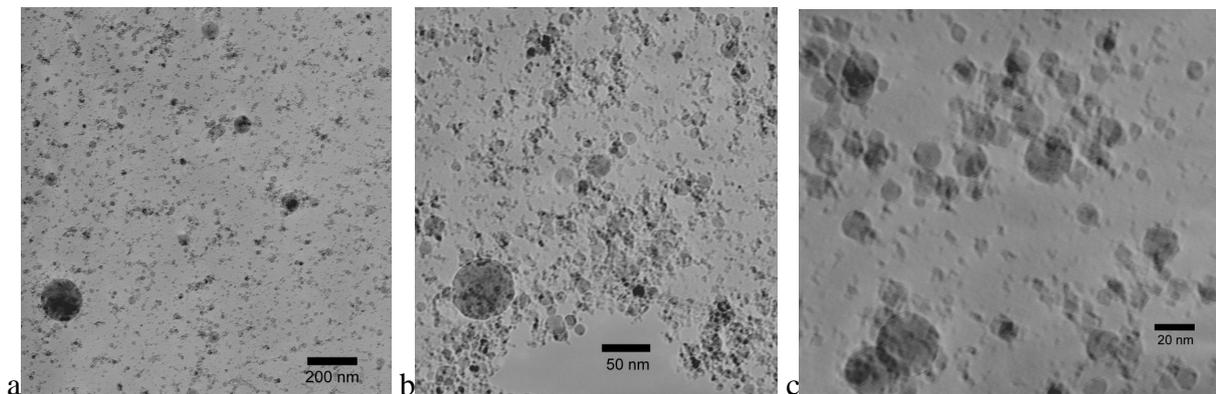


Figure 6.a, b and c. Overall TEM-graph of the nanoparticles collected from the flame before entering the surface of the ceramic tiles. The particles are located on the Carbon film supported by a Cu-grid. The spherical particles in between the nanoparticles are residual particles, i.e. remaining original liquid droplets, converted via liquid-to-solid reactions. Small dark dots in Figure 6c are silver (TUT)

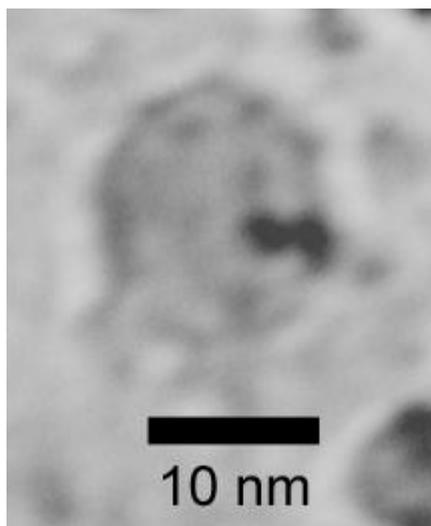


Figure 7. Titania particle ($d_p > 10\text{nm}$) with small silver particles (darker ones) on top (TUT)

TEM analysis detected the silver particles verifiably (Fig 8 and 9). Also the crystalline form of the titania particles was investigated. We noted that there are also small titania particles ($d_p < 20\text{ nm}$) of rutile (Fig. 10). This is very rare as the crystalline form of titania in small particles favours anatase (Fig. 11).

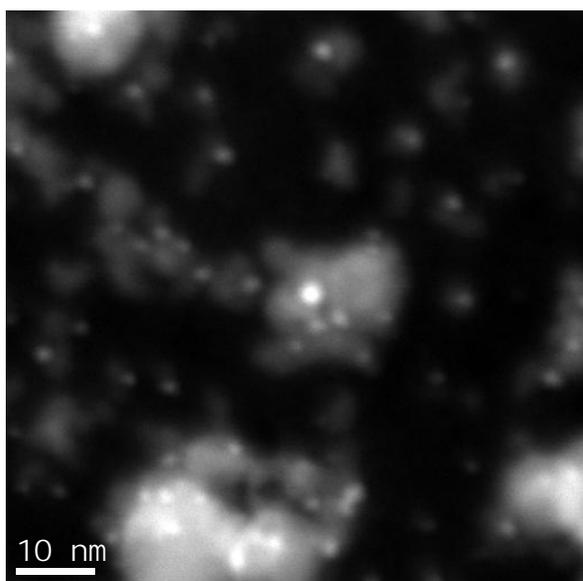


Figure 8. High Angle Annular Dark Field Image of the TiO₂-Ag nanocomposite Particles (Ag \leftrightarrow small bright spots) (LTH)

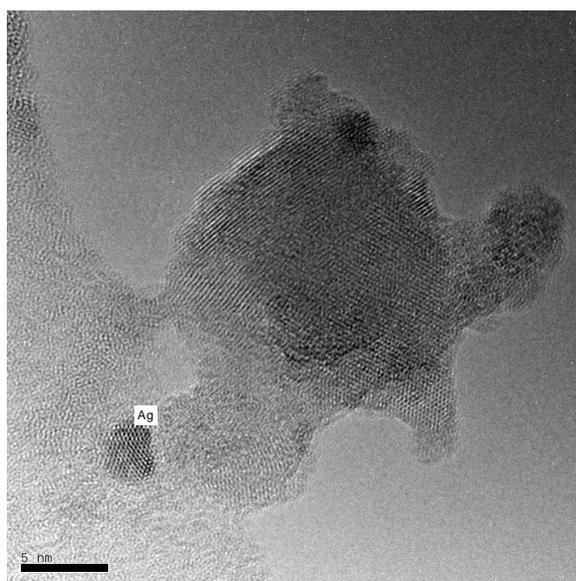


Figure 9. TEM image of a separate silver particle. (bar = 5 nm) (LTH)

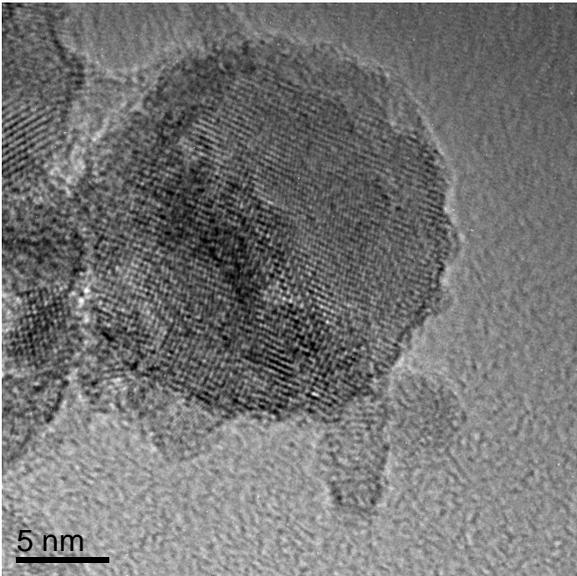


Figure 10. TEM image of rutile [100] particle (LTH)

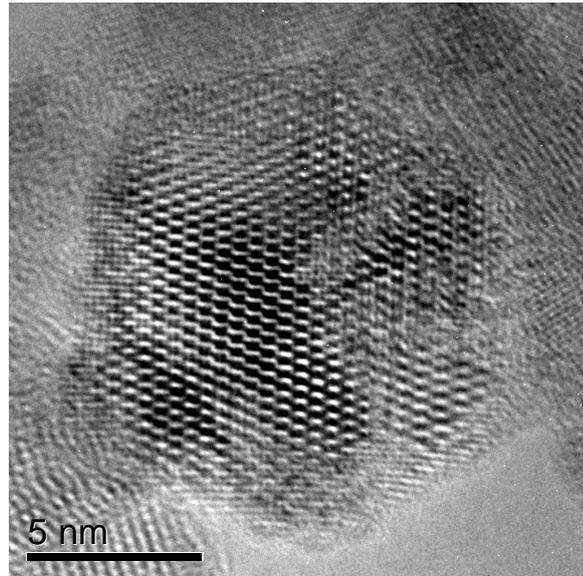


Figure 11. TEM image of anatase [100] particle (LTH)

As a result of the analysis, the titania particles can be divided to three size modes:

- 1) **Particles of ~ 10 nm**, The actual nanoparticles which cover the surface and contribute mostly to the photoactivity. Contain mainly anatase.
- 2) **Particles of ~ 100 nm**. The spherical particles in e.g. figure 6. According to our recent paper, these are residual particles formed by liquid to solid reactions, the contain mainly rutile.
- 3) **Particles of 1-10 μm** . The ‘white’ larger particles (see e.g. Figure 20). Assumed to be either generated from large agglomerates transported through the flame or from the largest droplets from the spray. When realized, this feature was taken care of and the extra particles were eliminated from the process during this project.

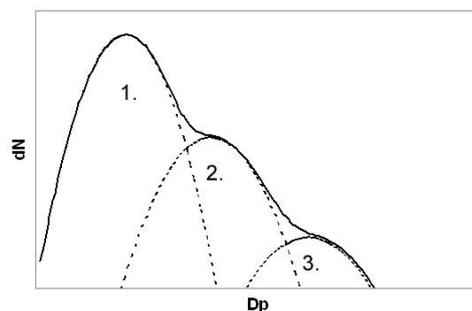


Figure 12. A schematic particle number size distribution of the three different modes of titania particles generated by LFS. The few nanometer sized silver particles, smaller than Mode 1, will form a fourth mode in the process.

All of these are mostly titania. Small silver particles were not visible all the graphs, especially SEM graphs. But they could be seen using the high resolution TEM. We also see the silver in the elementary analysis (EDS) combined with the transmission electron microscope (TEM) for the

samples taken from the flame. But, the ceramic tiles are difficult, since they contain quite much of aluminum, which disturbs detection of silver. To see the really nanosized silver particles on the substrates, is an extremely challenging task.

Structure of coatings

Overall look at the coated samples.

Plain float glass samples were coated in order to have a reference for the ceramic tiles. The float glass samples also provide information how the actual glaze will be coated. Therefore, the coated float glass samples were analyzed for optical properties. Some of the coating parameters create little opacity on the glass (Fig. 13). The transmission of the light is therefore greatly varied in samples. This might be due to larger amount of titania particles in the coatings. However, most of the samples are quite clear.

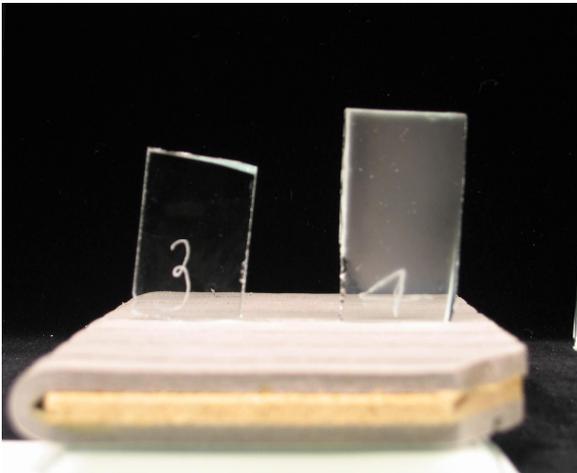


Figure 13. Different opacities of the coated samples. (Glafo)

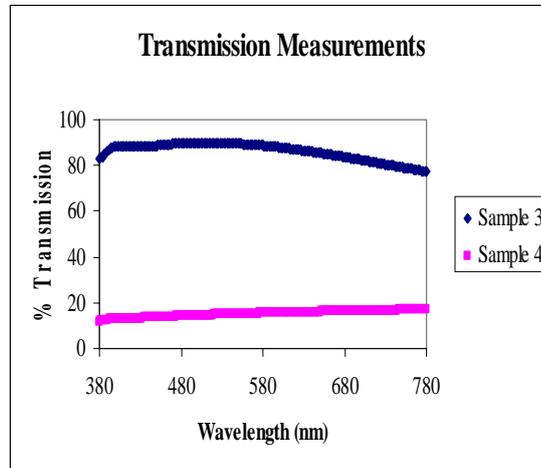


Figure 14. Transmission of light in different samples. (Glafo)

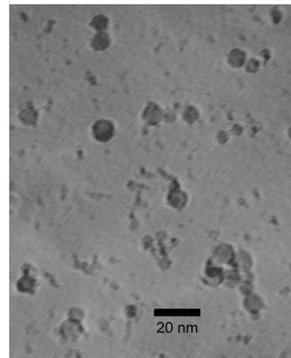
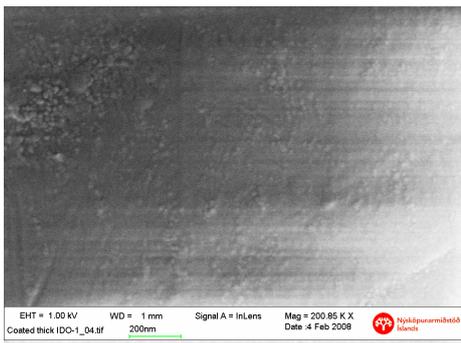
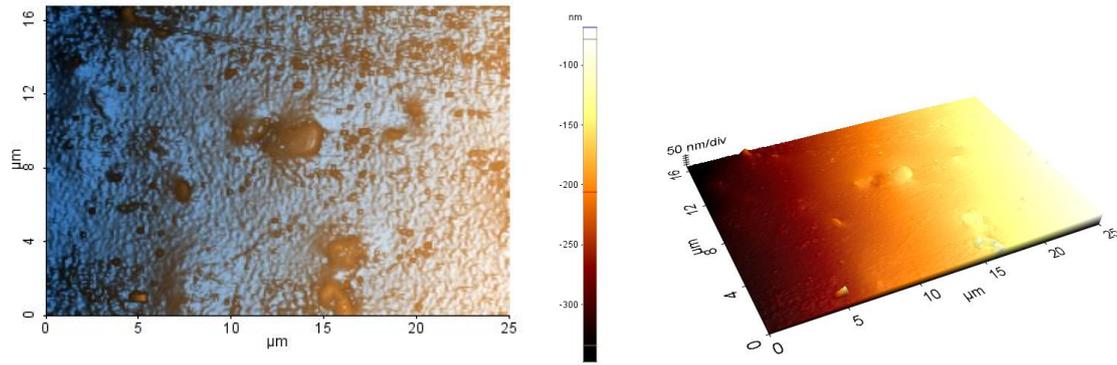


Figure 15. a,b,c & d. Sample 1 IDO-1 (IceTec)

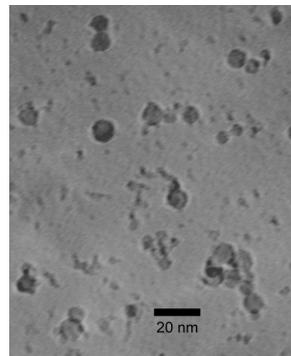
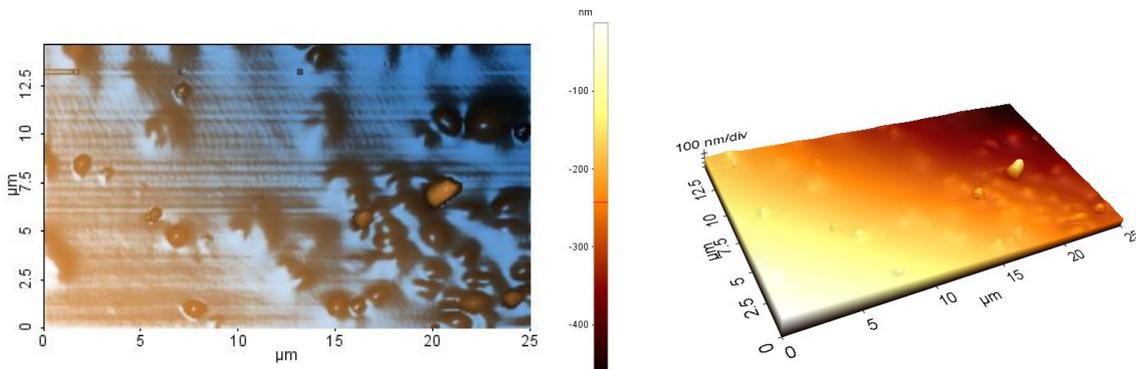


Figure 16. a,b,c & d. Sample 2 IDO-2 (IceTec)

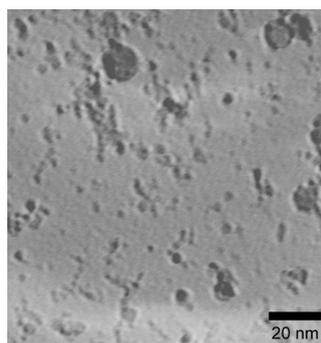
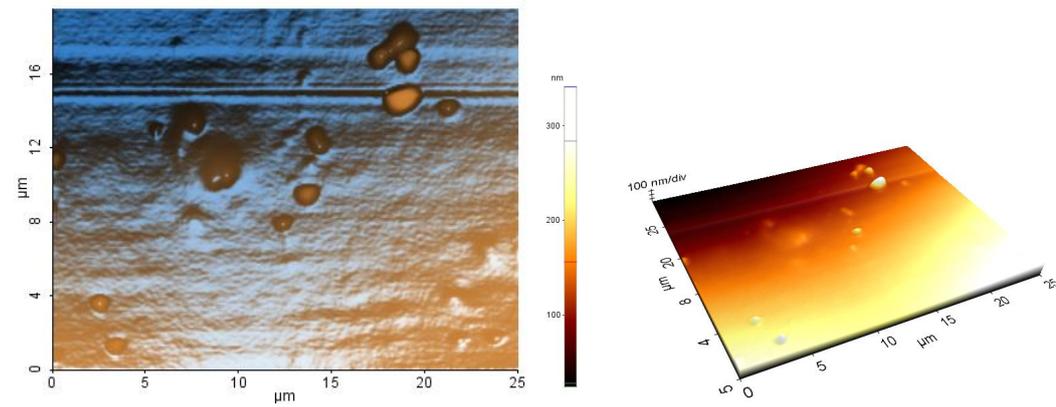


Figure 17. a,b,c & d. Sample 3 IDO-3 (IceTec)

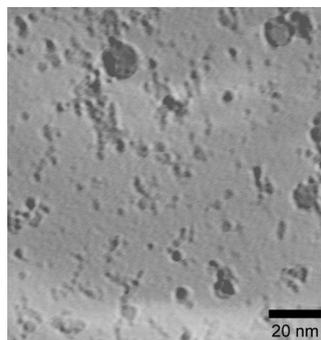
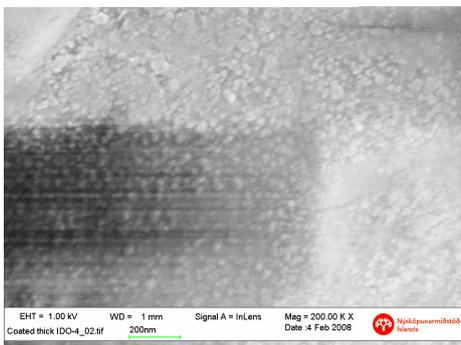
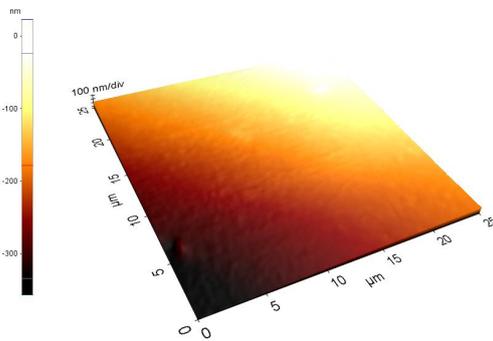
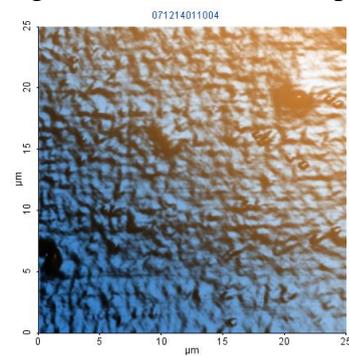


Figure 18. a,b,c & d. Sample 4 IDO-4 (IceTec)

Also the SEM analysis shows that the coating covers 100 % of the surface (Fig. 19). The particles are around 10-20 nm and there are some larger residual particles of 50-200 nm. The surface is totally covered with this cauliflower-shaped particulate matter even after wiping the surface in order to remove the loose particles. Therefore, it can be said that the coating is well attached on the surface. EDS analysis of the coatings showed even percentages of Ti and O all over the samples. This result tells that the coatings really consist of titanium dioxide as the TEM analysis of individual particles suggested. The nanocoating can be observed also in Figure 20 as a thin background all over the analyzed area.

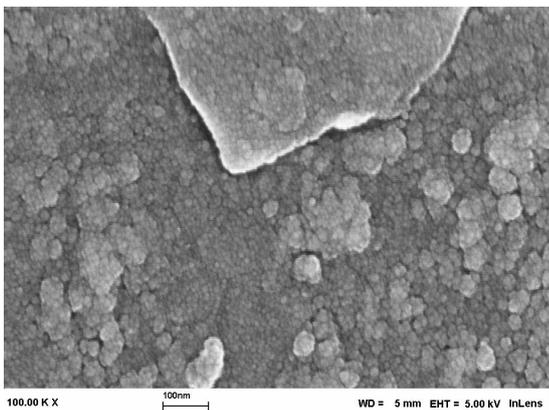


Figure 19. Cauliflower-shaped TiO₂ coating of 100 % coverage. (ÅÅ)

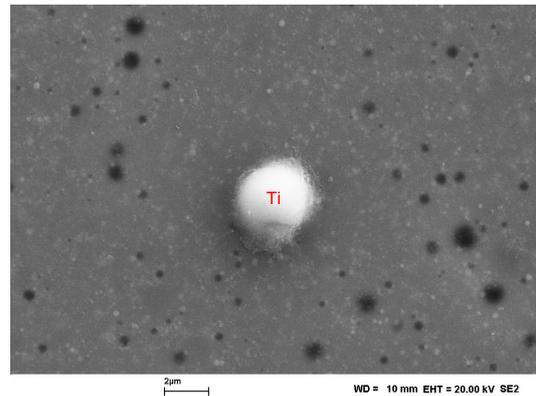
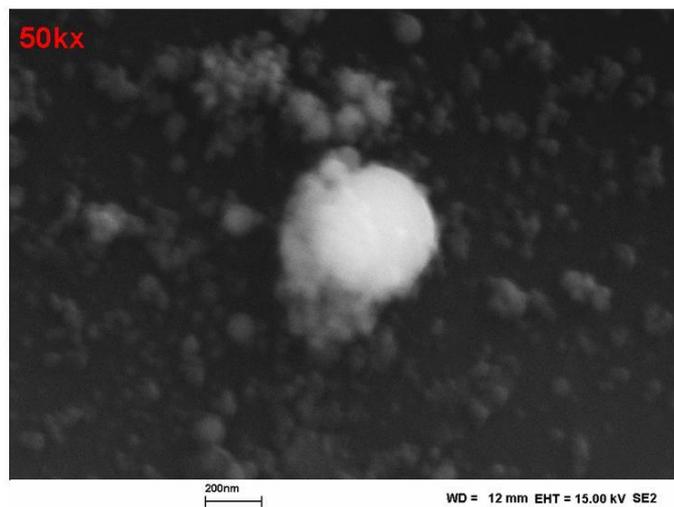


Figure 20. Large over micron sized TiO₂ particle. (ÅÅ)

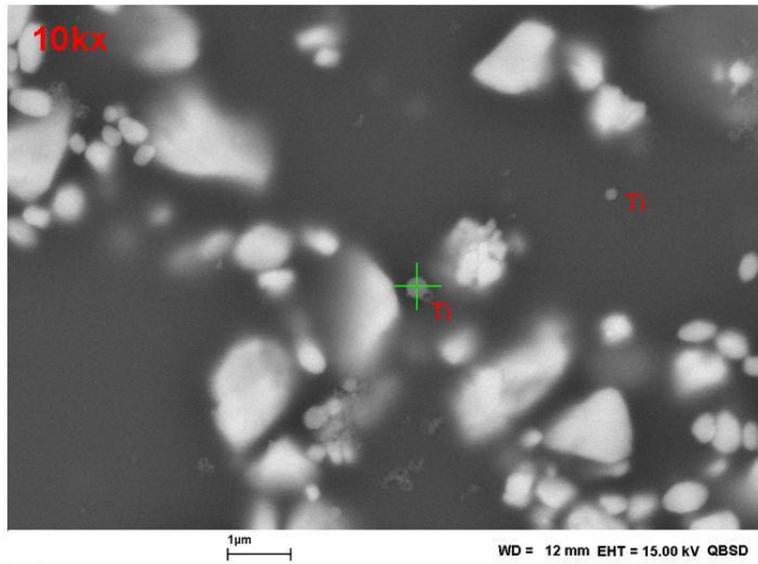
In the first test run, there were over micron sized particles every here and there in the sample detected by SEM (Fig 20). These large particles were formed via hydrolysis of precursor solution before usage. A sieve for 1 μm was installed in the liquid line and this removed all these over micron sized particles in the coatings in test runs 2 and 3. SEM graphs show the morphology of the tile surface. These results are demonstrated by Figures 21, 22 and 23.



(3A2)
t:550 °C
production rate: 50 mg/min TiO₂ + 0.05 mg/min
distance: 130 mm

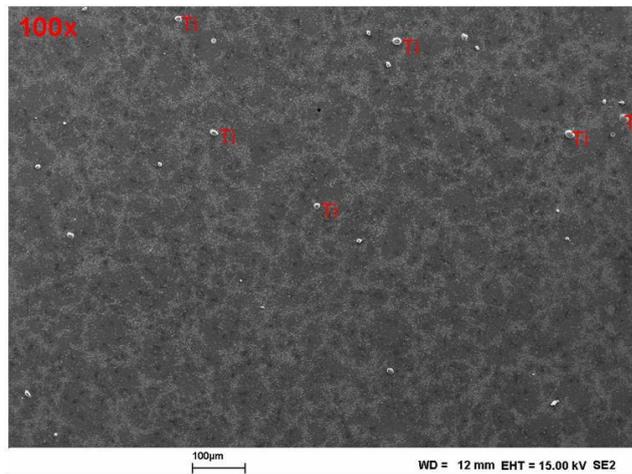
Figure 21. A large magnification showing the nanoparticle coverage of the surface of 3A-sample (special glaze developed in ÅÅ). In the middle, one spherical 'residual particle' is seen, having also

been coated by smaller nanoparticles. Note, silver particles are present here, but not visible for SEM. (ÅÅ)



(K1)
 t:500 °C
 production rate: 50 mg/min TiO₂ + 0.05 mg/min
 distance: 130 mm

Figure 22. SEM-graph. The white large crystals are zirconia, used in the glaze. Some residual particles have been identified to contain Titanium (Ti) (ÅÅ)



(K2)
 t:550 °C
 production rate: 50 mg/min TiO₂ + 0.05 mg/min
 distance: 130 mm

Figure 23. A smaller magnification. The micron-sized larger particles are visible as white spots.(ÅÅ)

Based on the experiments, it can be stated that the matt surfaces collect particles more efficiently than the glossy surfaces. Even glossy surfaces do have material attached on them.

Microscopy (SEM) with elemental analysis (EDS) shows :

- little amount of titanium
- but no visible peak of silver (1% wt of TiO₂)
- => amount of deposit small

Performance of the Product

Water contact angle

The coating increases hydrophobicity of the surfaces. Water contact angle tests showed that the contact angle is increased by 20 ° in the coated samples compared with the reference tiles (Fig. 24). Also in some coating parameters the contact angle was decreases below the reference when the sample was illuminated with UV-light (Fig. 26).

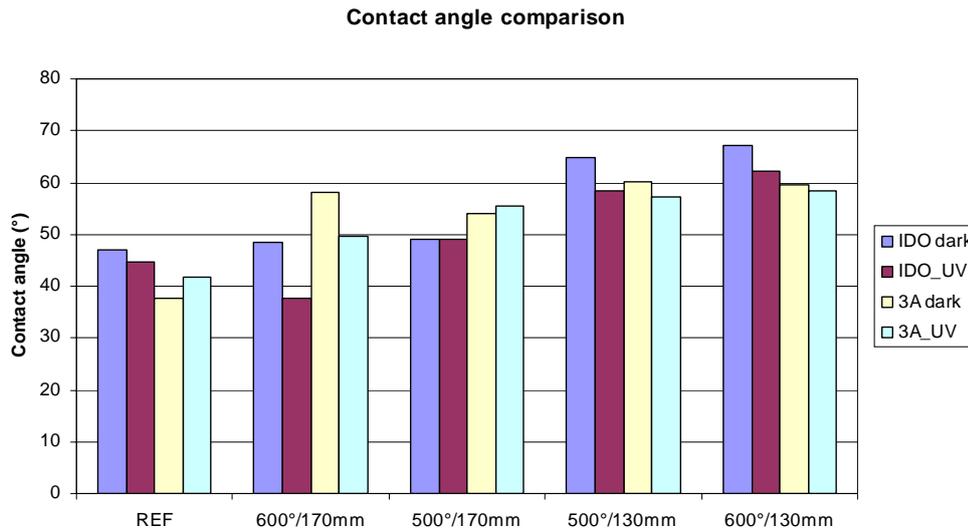


Figure 24. Water contact angles for different process parameters and tiles (TUT).

The water contact angle of the coatings was also measured as a function of time of the UV-illumination. As Figure 25 shows, the contact angle decreases with time. However the contact angle is still quite high, which is apparently due to the small amount of material on the surface.

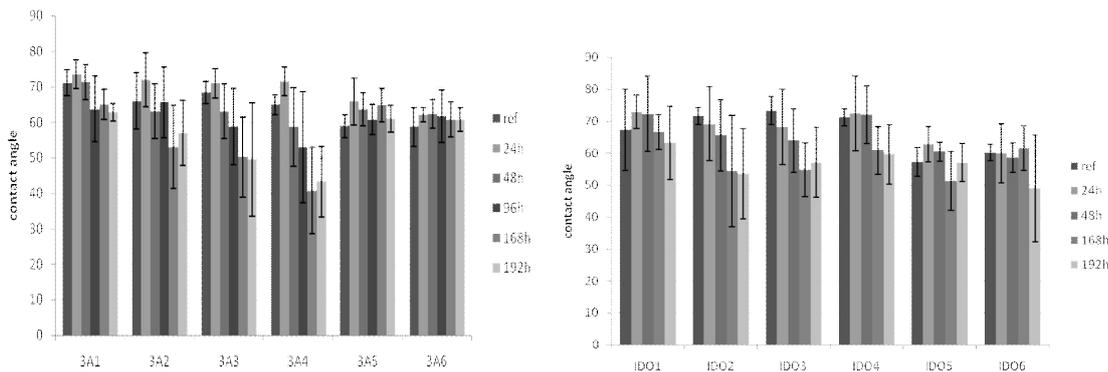


Figure 25. Contact angle as a function of time for various coatings (ÅA)

The confocal microscopy analyses reveal that the surface roughness is unaffected by the coating process. In Figure 26, we present an average of 6 measurements. It can be seen that the surface of the tile is as smooth as in the reference. The roughness is although somewhat dependent on the coating temperature as the surface has a slightly larger roughness in samples 1 and 4, which were coated in 600 °C compared with samples 2 and 3 which were coated in 500 °C. Also the roughness is slightly smaller in cases 2 and 3 when compared with the reference.

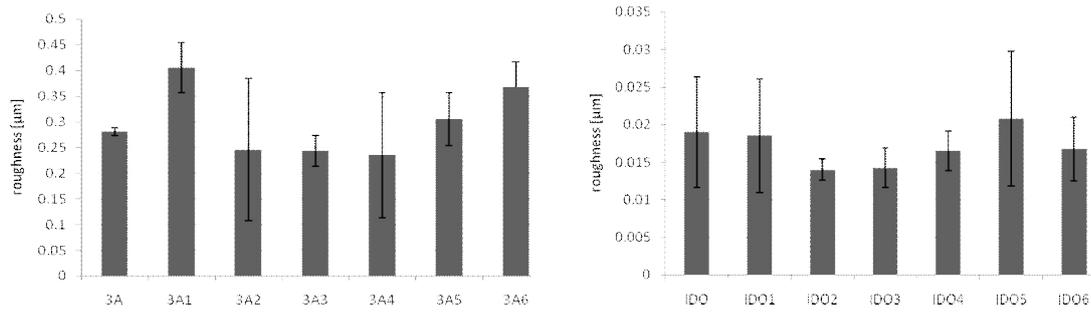


Figure 26. Surface roughness of different coatings. (Å)

Photocatalytic activity

Methylene blue degradation tests show that the coatings are capable of degrading methylene blue (Fig. 27). However, the degradation rate is not very high compared to coatings by other methods. This is, again, due to the amount of the material in the coating. It is evident that the amount of the material on the surface has a large impact on the degradation rate. In previous projects, these kinds of coatings have been applied on stainless steel surfaces in laboratory scale. Even there, the methylene blue degradation rate has not been a good indicator of the bacteria reduction capability of the coatings. So, this does not mean that the coating cannot be of high-quality in photocatalysis.

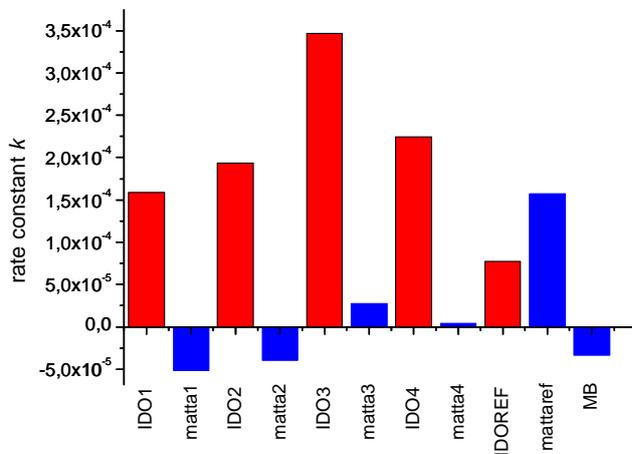


Figure 27. Degradation rate constants for different coatings.(UH/LIC)

Biofilm removal

The model bacteria *Pseudomonas Aeruginosa* grows in wet conditions, as in swimming pools. It is the main cause of eye infections for professional swimmers. In Finland the limit for the number of *P. Aeruginosa* cells in public baths is zero (below detection limit) in order to have good water quality. The bacteria is not previously used in testing these kinds of surfaces. Therefore, the growth conditions had to be optimized for the surfaces. In the first samples from test run number 2, the conditions were optimized on ordinary laboratory glass used in microscopy. However, the chemical composition of laboratory glass is different from the glazings. The bacteria grew well on laboratory

glass, but did not grow even on the non-coated reference sample. Thus, the coated samples did not have a chance to outshine the reference (Fig. 28).

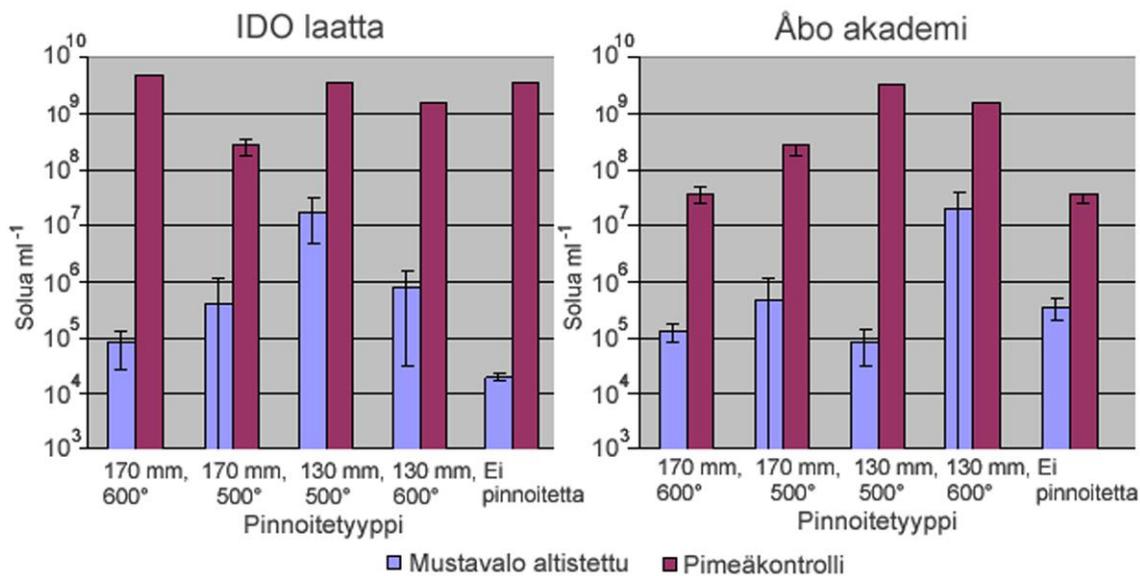


Figure 28. Biofilm reduction results for the coatings.(UH/MB) In both figures, the rightmost set denotes uncoated reference.

One of the essential benchmarks of the FUNCOAT-project was determination of the antibacterial property of the prepared coatings. This turned out to be a challenging task. In previous projects the liquid flame spray coated glass and even metal surfaces were verified to be antibacterial by the known model bacterium used in biofilm destruction studies, *Deinococcus geothermalis* (E50051). Thus, film of bacteria was removed when surfaces were exposed to UV-radiation.

Deinococcus geothermalis, however, is not included a standard procedure for surface testing in ordinary bathroom use. Actually real standardized procedure does not even exist for these surfaces, yet. Therefore, more work should be targeted in creating a standard for a biofilm removal method for analyzing thin films and nanocoatings. In the FUNCOAT-project, *Pseudomonas aeruginosa* (PAO1) was used- (DMSZ-base, transferred for the study from Germany). It is also used generally in biofilm research. In the tests, preparations were for ordinary float glass reference surfaces, where the attachment was maximized by searching optimal ferric ion concentration in water. It turned out, that in the same conditions with the FUNCOAT samples, the bacteria populations did not grow on the tiles in the first place, because of the non-optimal growth circumstances.

This led us to search for pre-conditioning of the samples, extending even to attachment of extra dirt on the surfaces, to enable bacterial attachment prior to UV-treatment.

Coating Thickness

A method of leaching of material was developed (Fig 29). By this method the depth profile of coating and the amount of coating material in surface can be studied (Fig 30). The samples have a very thin layer of titania and silver on the surface.

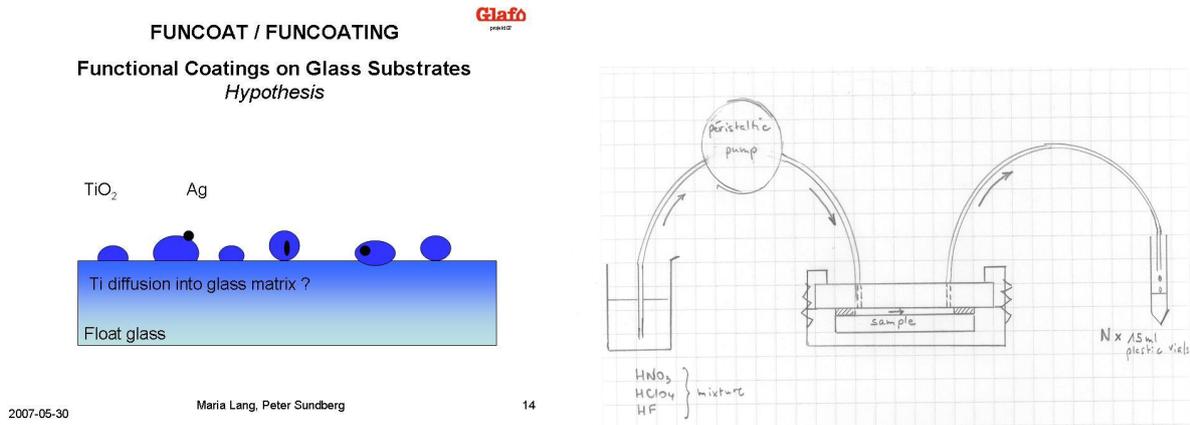


Figure 29. a) Background behind the depth analysis, b) Device and method to determine the amount of material in coatings on the float glass samples. (Glafo)

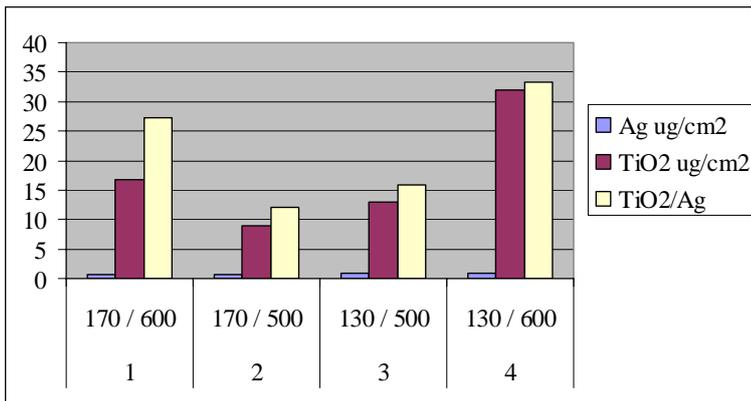


Figure 30. Results of the material analysis (Glafo)

Miscellaneous

Contribution of partners

Analyses:

Tampere University of Technology: Co-ordination, sample preparation, overall analysis, TEM+EDS+SAED, Water contact angle

Åbo Akademi University, Process Chemistry Centre, Overall analysis of the coatings, particle size, roughness (confocal microscopy, SEM, soiling tests. Supplying the ceramic tile materials

Lund University: Nanoscale microscopy

Glafo: Standard based tests on the tiles, depth profile analysis

IceTech: AFM & SEM-analysis on the tiles

University of Helsinki, Lab. Inorganic Chemistry: Tests for photocatalytic activity of surfaces

University of Helsinki, Dept. Microbiology: Biofilm removal tests

Micronova: Attachment and number density of nanoparticles on the tiles 'in-situ'.

The contribution of Micronova in the NICE project Funcoat: Micronova participated in the Funcoat project. They analysed TiO₂-Ag coated silicon wafer samples. The goal was to obtain information about the attachment of the particles on the surface. The coated samples were cleaned by thoroughly wiping the surface with a cloth in order to remove the loosely adhered particles. Micronova analysed the samples using Scanning Electron Microscopy (SEM). It was assumed that the resolution of the SEM would be sufficiently high to distinguish separate particles on the surface. Micronova has developed a computational model to get the surface coverage of the particles from a SEM image. The coating consisted of such small particles that the resolution of the SEM was not sufficient enough to get high quality images for the computational model and therefore the analysis failed. After noticing that that the task was beyond the performance of the device and method, and the results would not be of sufficient quality, they decided to suspend from the project.

Company contribution:

Beneq Ltd: Coating process, precursors

IDO Bathroom: Supplying the ceramic tile materials

Crystal Fibre: Burner improvement via a ceramic nozzle

Publication activities

Conference papers

1. J.M. Mäkelä, H. Keskinen, M. Aromaa, L. Hupa, M. Piispanen, K. Deppert, S. Persson, M. Lang, G. Gunnarsson, J. Pimenoff, T. Kronberg, V. Pore, M. Ritala, M. Leskelä, M. Raulio, M.S. Salkinoja-Salonen and V.-M. Airaksinen, A Nordic project on enhanced functionality of self-cleaning and antibacterial ceramic-metal surface coatings (FUNCOAT), Abstract to Nanotech Northern Europe, 27.-29 March 2007, Helsinki, Finland.
2. J.M. Mäkelä, H. Keskinen, M. Aromaa, L. Hupa, M. Piispanen, K. Deppert, S. Persson, M. Lang, G. Gunnarsson, J. Pimenoff, T. Kronberg, V. Pore, M. Ritala, M. Leskelä, M. Raulio, M.S. Salkinoja-Salonen and V.-M. Airaksinen, A Nordic project on enhanced functionality of self-cleaning and antibacterial surface coatings (FUNCOAT), Abstract to European Ceramic Society, 17.-21.6.2007, Berlin, Germany
3. M. Lang et al. Poster at NGF ("Nordic" Society for Glass Technology) week 21/07, Sweden.
4. M. Aromaa, H. Keskinen, J.M. Mäkelä, M. Piispanen, L. Hupa, K. Deppert, S. Persson, M. Lang, P. Sandberg, G. Gunnarsson, J. Pimenoff, T. Kronberg, V. Pore, M. Ritala, M. Leskelä, and M. Raulio, Characterisation of industrial aerosol nanoparticle generation process, Abstract to European Aerosol Conference, 9.-14.9.2007 Salzburg, Austria
5. J.M. Mäkelä, H. Keskinen, M. Aromaa and J.Pimenoff Liquid flame spray method to generate thin nanoparticle coatings, Abstract to Nanotech Russia, 12.-13.9.2007, Helsinki, Finland
6. M. Aromaa, H.Keskinen, J.M. Mäkelä and J. Pimenoff, Thin nanoparticle coatings generated by Liquid Flame Spray method, Abstract to European Materials Research Society Fall Meeting 2006, 17.-21.9.2007 Warsaw, Poland
7. M. Aromaa, J.M. Mäkelä, H. Keskinen, M. Piispanen, L. Hupa, K. Deppert, J.B. Wagner, L.R. Wallenberg, J. Pimenoff, M. Lang, S. Persson, P. Sundberg, T. Kronberg, V. Pore, M. Heikkilä, M. Ritala, M. Leskelä, M. Raulio, M.S. Salkinoja-Salonen and V.-M. Airaksinen, Optimization Of An Industrial Aerosol Nanoparticle Generation Process For Creating Photocatalytic And Anti-Microbial Coatings, Abstract to AIChE (American Institute of Chemical Engineers) Annual Meeting, 4.-9.11.2007, Salt Lake City, Utah, USA
8. M. Piispanen, M. Aromaa, H. Keskinen, M. Raulio, S. Areva, J.M. Mäkelä, M.S. Salkinoja-Salonen and L. Hupa Liquid Flame Spray and sol-gel titania coatings on glass with self-cleaning and bactericidal properties, Abstract to The International Conference on Coating on Glass and Plastic (ICCG7), 15.-19.6.2008, Eindhoven, The Netherlands.

Theses

PhD Helmi Keskinen, Tampere University of Technology, Institute of Physics, (June 2007) (partly FUNCOAT)

M.Sc. Mikko Aromaa, Tampere University of Technology, Institute of Physics, (November, 2006).

Coming theses (to be partly based on the results of the FUNCOAT-project)

PhD Minna Piispanen, Åbo Akademi – Process Chemistry Centre, Estimated dissertation, 2009

PhD Mikko Aromaa Tampere University of Technology, Institute of Physics, estimated dissertation 2009

Summary

In this project, a variety of ceramic tiles were coated with titanium oxide- silver nanoparticles. The goal was to achieve a smooth thin coating with a functional performance, with both photocatalytic and antibacterial properties, and without altering other properties of the tiles, such as colour. We succeeded in fabricating the fine quality multicomponent nanocoating on the tiles. In the project, a high quality analysis of the nanoparticles from the process and of the particles on the coating were obtained.

The second goal of the project was to verify the functionality of the fabricated thin coatings on the ceramic tiles. This turned out to be more challenging task than what was originally anticipated. The surfaces were hydrophobic, and became hydrophilic with UV-illumination. It came apparent that the coatings were photocatalytic, but due to the small amount of material -- approximately one monolayer of silver doped titania nanoparticles on the tiles -- the obtained photocatalytic reaction rate coefficients were smaller than originally expected. Also, it turned out that standard testing procedures for the capability of the prepared surfaces for biofilm removal, do not presently exist for thin films.

All in all, a vast amount of scientific information on the fabricated multicomponent nanocoatings was gained during the project. The surfaces were functional, but the effect was too small for a present industrial significance. For commercial breakthrough, the topic still requires much more research and development.

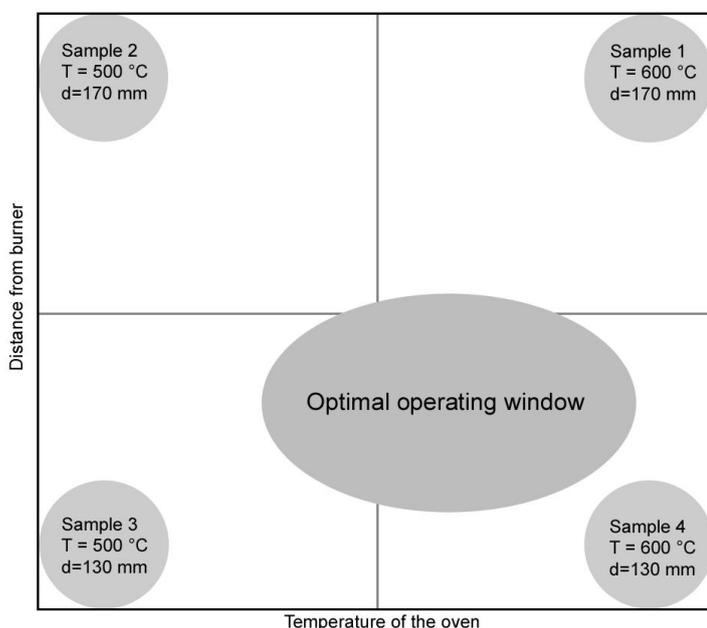


Figure 31. A conclusive schematic based on the experimental results of the project. The optimal operating window is shown in the middle.

References

- Arstila, H., Hupa, L., Vedel, E., Ylänen, H., Hupa, M., The sintering range of porous bioactive glasses *Glass Technol.*, 46 (2005) 138.
- Arstila, H. Vedel, E., Hupa, L. Fibers and porous implants by controlling the phase separation of bioactive glasses. Accepted, *J. Eur. Cer. Soc.* (2006)
- Fröberg, L., Kronberg, T., Hupa, L., Hupa, M. Influence of firing parameters on phase composition of raw glazes. Accepted, *J. Eur. Cer. Soc.* (2006)
- Fröberg, L., Kronberg, T., Törnblom, S., Hupa, L. Chemical durability of glazed surfaces. Accepted, *J. Eur. Cer. Soc.* (2006)
- Gross K.A., J. Tikkanen, J. Keskinen, V. Pitkänen, M. Eerola, R. Siikamäki & M. Rajala, 1999. Liquid based flame spraying on hot glass surfaces, *J. Thermal Spray Tech.* 8, 583.
- Hupa, L., Bergman, R., Fröberg, L., Vane-Tempest, S., Hupa, M., Kronberg, T., Pesonen-Leinonen, E., Sjöberg, A.M. Chemical resistance and cleanability of glazed surfaces, *Surface Science*, 584 (2005) 113.
- Keskinen H., J. M. Mäkelä, M. Vippola, M. Nurminen, J.K. Liimatainen, T. Lepistö, & J. Keskinen, 2004a. Generation of silver/palladium nanoparticles by liquid flame spray, *J. Mat. Res.* 19, 1544.
- Keskinen H., J.M. Mäkelä S. Hellsten, M. Aromaa, E. Levänen & T. Mäntylä, 2005. Generation of titania nanoparticles by liquid flame spray for photocatalytic applications, *Electrochem. Soc. Proc.* 2005-09, 491.
- Keskinen, K., J.M. Mäkelä, M. Aromaa, J. Ristimäki, T. Kanerva, E. Levänen, T. Mäntylä and J. Keskinen, 2006, Effect of silver addition on the formation and deposition of titania nanoparticles produced by Liquid Flame Spray *Journal of Nanoparticle Research*, In Press 2006 (accepted 12/2005).
- Kuisma, R., Fröberg, L., Kymäläinen, H.R., Pesonen-Leinonen, E., Piispanen, M., Melamies, P., Hautala, M., Sjöberg, A.M., Hupa, L. Morphology and cleanability of uncoated and fluoropolymer, zirconia and titania coated ceramic glazed surfaces, accepted, *J. Eur. Cer. Soc.* (2006)
- Kronberg, T., Ritschkoff, A.C., Mahlberg, R., Mannila, J., Kallio, M., Vesa, A., Hupa, L. Soil-resistant surfaces for traditional ceramics. Accepted, *J. Eur. Cer. Soc.* (2006)
- Mäkelä J. M., H. Keskinen, T. Forsblom & J. Keskinen, 2004. Generation of metal and metal oxide nanoparticles by liquid flame spray process, *J. Mater. Sci.* 8, 2783.
- Mäkelä, J.M., S. Hellstén, J. Silvonen, M. Vippola, E. Levänen, & T. Mäntylä, 2006. Collection of liquid flame spray TiO₂ nanoparticles on stainless steel surface, *Mater. Lett.* 60, 530.
- Pitkänen, A., J. M. Mäkelä, M. Nurminen, A. Oksanen, K. Janka, J. Keskinen, H. Keskinen, J. K. Liimatainen, S. Hellstén and T. Määttä. Numerical Study of Silica Particle Formation in Turbulent H₂/O₂ Flame. *IFRF Electronic Combustion Journal*, Article Number 200509, December 2005
- Tikkanen J., K.A. Gross, C.C. Berndt, V. Pitkänen, J. Keskinen, S. Raghu, M. Rajala & J. Karthikeyan, 1997. Characteristics of the liquid flame spray process, *Surf. Coatings Tech.* 90, 210.



norden

Nordic Innovation Centre

Nordic Innovation Centre

Nordic Innovation Centre (NICe) is an institution under the Nordic Council of Ministers facilitating sustainable growth in the Nordic economies.

Our mission is to stimulate innovation, remove barriers and build relations through Nordic cooperation. We encourage innovation in all sectors, build transnational relationships, and contribute to a borderless Nordic business region.

We work with private and public stakeholders to create and coordinate initiatives which help Nordic businesses become more innovative and competitive.

Nordic Innovation Centre is located in Oslo, but has projects and partners in all the Nordic countries.

For more information: www.nordicinnovation.net