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Thin Film Coatings Prepared by Direct Thermophoretic Deposition of Flame-Made Nanoparticles

Gianluigi De Falco[a]*, Amalia Porta[b], Pasquale Del Gaudio[b], Mario Commodo[a], Patrizia Minutolo[a], Andrea D'Anna[c]

[a] Istituto di Ricerche sulla Combustione, CNR, Piazzale Tecchio, 80 - 80125, Napoli, Italy
[b] Dipartimento di Farmacia, Università degli Studi di Salerno, Via Giovanni Paolo II 132, 84084 - Fisciano (Sa), Italy
[a] Dipartimento di Ingegneria Chimica, dei Materiali e della Produzione Industriale, Università degli Studi di Napoli Federico II, Piazzale Tecchio, 80 - 80125, Napoli, Italy
gl.defalco@irc.cnr.it

This study reports the development of a one-step method for the production of thin film coatings made with metal oxide nanoparticles. An aerosol flame synthesis system is used to produce monodisperse, ultra-fine nanoparticles of different metal oxide, by changing the precursor fed to the flame. The flame reactor is a fuel-lean reactor of ethylene and air. Flame-synthesized nanoparticles are directly deposited by thermophoresis onto different substrate by means of a rotating disc. Substrates were mounted onto the rotating disc that repetitively passes through the flame. Convection due to the rotational motion cooled the substrates, on which particles were deposited as films by thermophoresis. Such a system allowed to obtain submicron coatings of different thickness and porosity, by varying the total time of deposition. Different substrates can be coated using this method, such as aluminum and steel plate. Particle and coating characterization is performed by means of Differential Mobility Analysis, Raman and X-Ray Diffraction spectroscopy, and UV-Vis absorption. A preliminary analysis of the antimicrobial activity of TiO_2 nanoparticle coatings produced with this method has been performed against *Candida Albicans*, and compared to that of commercial TiO_2 nanopowder. The results are promising for using titania films as protective coatings for applications where an antimicrobial activity is required, such as self-cleaning materials able to reduce microbial infections.

1. Introduction

The presence of microbial populations in any crowded indoor environment is often responsible for the spreading of different diseases, causing the degradation of air quality (Bellanger et al., 2009). Some of those microorganism are common indoor fungi such as *Candida Albicans,* which can be found on indoor and outdoor building materials, or bacteria like *Staphyloccoccus aureus and Streptococcus mutans*, which are found inside nosocomial environments (Verdier et al., 2014). Both fungi and bacteria possess the capability to form biofilms on walls, air ducts surfaces and plants, following mechanisms strictly related to their pathogenicity and environmental colonization (Kaeberlein et al., 2002). Innovative and more efficient sanitizing agents for environmentally contaminated surfaces can be obtained from nanomaterials (Campoccia et al., 2013). One of the most suitable nanomaterial to produce self-cleaning and antimicrobial coating layers of common material surfaces is titanium dioxide TiO_2, since it is characterized by a high photocatalytic activity, together with a lower biologically and environmentally toxicity with respect to silver and zinc oxides, which are mostly used for antimicrobial applications in the form of nanoparticles (Weir et al., 2012). Due to their optical properties, TiO_2 nanoparticles can produce reactive oxygen species (ROS) which are in turn able to damage outer and/or cytoplasmic membrane of microorganism (Armelao et al., 2007), making titania an excellent antimicrobial agent. Moreover, TiO_2 nanoparticles possess an increased surface area, which results in an improved photo-oxidation efficacy.
The advantages of producing nanoparticles via flame synthesis, compared to other synthesis method, are the continuous and direct operation, the high production rate, the fast processing time, the simplicity of manufacturing and collection, and the almost negligible generation of waste and by-products (Li et al., 2016).

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Moreover, nanoparticles produce via flame synthesis can be easily deposited by thermophoresis on appropriate substrates placed downstream of the flame synthesis burner, thus easily obtaining nanostructured films and coatings (Batchelor and Shen, 1985). Nano-TiO_2 thin films have been synthesized by the thermophoretic deposition method for several applications, such as photo water-splitting (Thimsen et al., 2008) and dye sensitized solar cells (Nikraz et al., 2012).
This work reports the development of a one-step method for the production of thin film coatings made with TiO_2 nanoparticles on aluminium substrates direct thermophoretic deposition. The ability of flame-made nanoparticle coatings to prevent fungi biofilm formation was tested by crystal violet (CV) assay and quantified by spectrophotometry. A comparison with coatings made of commercial TiO2 nanopowder was conducted. Moreover, the potential enhanced effect of UV irradiation on nano-coatings antifungal activity was investigated, since it is more representative of the natural conditions usually considered for passive devices.

2. Experimental

Titania nanoparticles were produced in an Aerosol Flame Synthesis (AFS) system. The flame reactor was a laminar premixed flame of ethylene and air (cold gas velocity=100 cm/s, equivalent ratio Φ=0.83), doped with a 0.3 M solution of titanium tetraisopropoxide (TTIP, Aldrich, 97%) dissolved into ethanol (ACS reagent, ≥99.5%). More details on the AFS system and the experimental conditions are reported in previous works (De Falco et al., 2016; De Falco et al., 2017). Thin film of nanoparticles were obtained by thermophoretic deposition on a rotating circular disk (diameter 30 cm, thickness 0.35 cm), which was kept in rotation by means of a brushless c.c. geared motor (Crouzet 80-035-508), designed according to Memarzadeh et al. (2011). The substrates to be coated were 16 mm diameter aluminum AA2024 circular substrates, with a thickness of 3 mm, inserted onto six flat slots derived into the rotating disk. The rotation of the disk allowed the substrates to be repetitively inserted into the flame, and particles to be deposited by thermophoresis, forming a uniform coating on the substrate. By varying the total deposition time, different thicknesses of the coating can be obtained.
Raman spectroscopy was performed using a Horiba XploRA Raman Microscope System (Horiba Jobin Yvon, Japan) with an excitation wavelength of λ=532 nm, while UV-vis absorption spectra were acquired on nanoparticle coatings deposited on quartz substrates, by means of an Agilent UV-visible 8453 spectrophotometer.
In order to evaluate the antimicrobial activity of the TiO_2 films, the inhibition of biofilm formation of *Candida albicans* (ATCC SC5314) was tested. Bacteria cells (108 cellule/mL) were suspended in Mueller-Hinton Broth (MHB), aliquoted in a 12-wells plate (1.5 ml/well) containing the aluminum substrates and incubated overnight at 37°C. Aluminum substrates were moved in a new 12-well plate and washed three times with PBS to remove non adherent cells. The remaining biofilm were dried and stained with crystal violet solution 0.3% (w/v) for 15 min. The unbound crystal violet was removed rinsing with water, and the substrates were then photographed in order to qualitative compare tested substrates. Finally, the biofilm mass was quantified by solubilizing the CV with 200 μl of acetic acid (33% v/v), and measuring absorbance at a wavelength of 595 nm using a spectrophotometer.
The effect of UV irradiation was investigated by irradiating substrates at a wavelength of 365 ± 1 nm for 0, 2, 3, 5, 15 and 30 minutes, with light intensity at the coating surface adjusted to 1.35 mW/cm^2 (Collimated LED light M365LP1, Thorlabs, Inc., Germany). Immediately after irradiation, substrates were placed into 12-wells plates, each plate containing the microorganism to be tested. An uncoated aluminum substrate was used as a positive control.
The antimicrobial activity of flame-synthesized titania nanoparticle coatings was compared to that of commercial titania nanoparticles deposited by solvent evaporation technique. To this aim, reference coatings were produced by homogenous suspending a proper amount of Aeroxide® TiO_2 P25 (Sigma-Aldrich, Switzerland) in acetone, which was then deposited drop by drop on an aluminum substrate. A flux of N_2 at room temperature was then used at room temperature to remove acetone, in order to obtain a coating equivalent in TiO_2 mass to those obtained by AFS.

3. Results and discussion

The properties of flame synthesized nanoparticles and thermophoretic-deposited coatings have been characterized and reported in previous works (Liberini et al., 2016; De Falco et al., 2017).
Mean particle diameter was measured by means of a Scanning Mobility Particle Sizer and found to be <Dp>=3.5 nm, with an high degree of monodispersion. XRD and Raman spectroscopy were used to determine the phase composition of nanoparticles, which were found to be pure anatase, and to point out that no changes in particle phase are due to the deposition system. From UV-Vis absorption measurements, the

porosity of deposited films was evaluated to be almost constant for different deposition times and equal to 0.985. Three samples with different thickness were produced at different total deposition times, and characterized by means of an optical microscopy technique based on confocal microscopy. The thickness of the three samples was measured to be about 0.7 μm for a total deposition time of 10 s, 3 μm for a total deposition time of 30 s and 5 μm for a total deposition time of 60 s. A simple model for a theoretical evaluation of flame-made particle film growth rate by thermophoretic deposition has been proposed by Madler et al. (2006). The model assumes a constant stagnation gas layer in front of the substrate in which particle transport by axial convection is smaller than transport by thermophoresis and diffusion, and a linear concentration of both particles and temperature can be assumed. This model was applied to calculate the film growth rate as a function of the total deposition time, from which thickness of the layer can be derived. Calculated and measured film thicknesses are reported in Figure 1, showing a good agreement between measurements and model prediction.

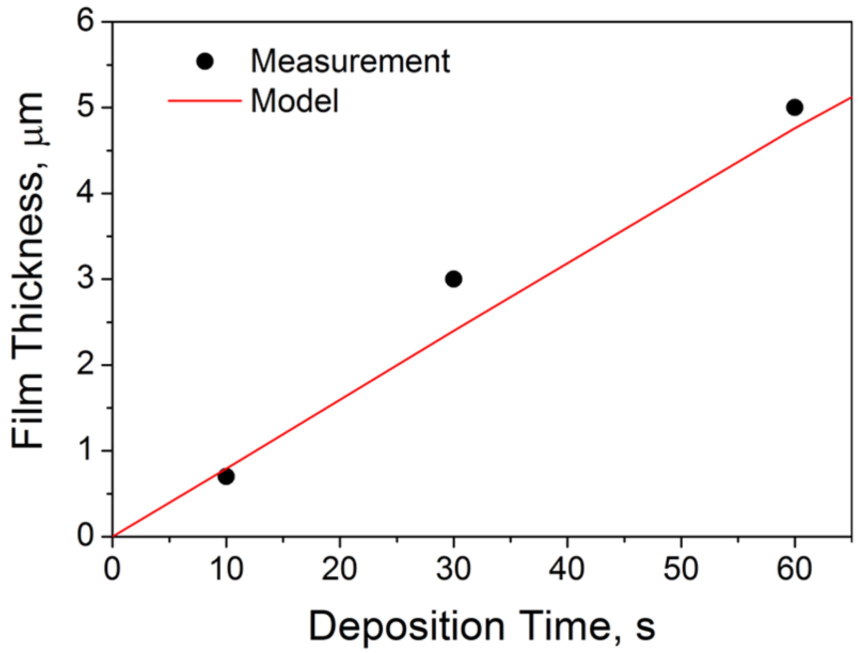

Figure 1: Calculated film thickness (line) and measured film thickness (points) as a function of total deposition time.

The performances of AFS TiO_2 coatings in terms of antifungal activity were compared to that of reference coated aluminum disks, produced by solvent evaporation technique, using the same mass amount of titanium dioxide P25 powder as the AFS TiO_2 disk obtained with a total deposition time of 30 s.
Figure 2 reports the Raman spectra acquired on the P25 coating and the AFS TiO_2 coating. In the AFS TiO_2 coating spectrum, five peaks are detected, corresponding only to the Raman bands of anatase (Balachandran and Eror, 1982). On the other hand, in the P25 TiO_2 coating spectrum, a peak corresponding to Raman band of rutile can be also observed, showing that commercial TiO_2 is constituted by a mixture of anatase and rutile, rutile being the predominant phase, while AFS TiO_2 is pure anatase.
UV-Visible absorption spectra of AFS TiO_2 coating and P25 coating are shown in Figure 3. Both spectra show a high absorbance in the UVA/UVB region with comparable maximum absorption intensities, confirming that the same mass amount of titania was deposited on both substrates. The absorption of P25 coating is slightly shifted to higher wavelength, due to the presence of a little amount of rutile in the phase composition of P25 titania (Ruzmanova et al., 2105), which is characterized by a lower band-gap with respect to anatase (Liu et al., 2012).

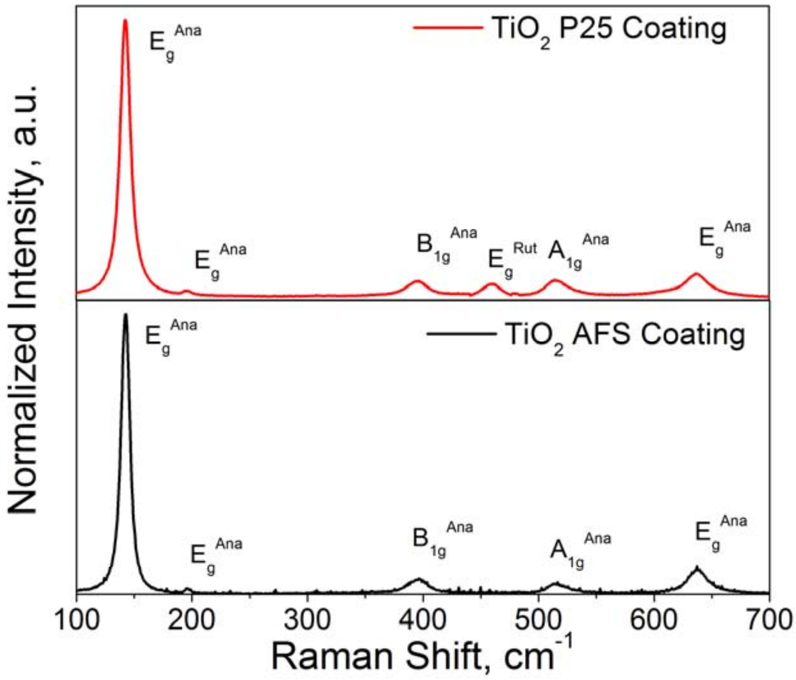

Figure 2: Raman spectra of P25 coating prepared by solvent evaporation technique and AFS TiO_2 coating obtained with a total deposition time of 30 s.

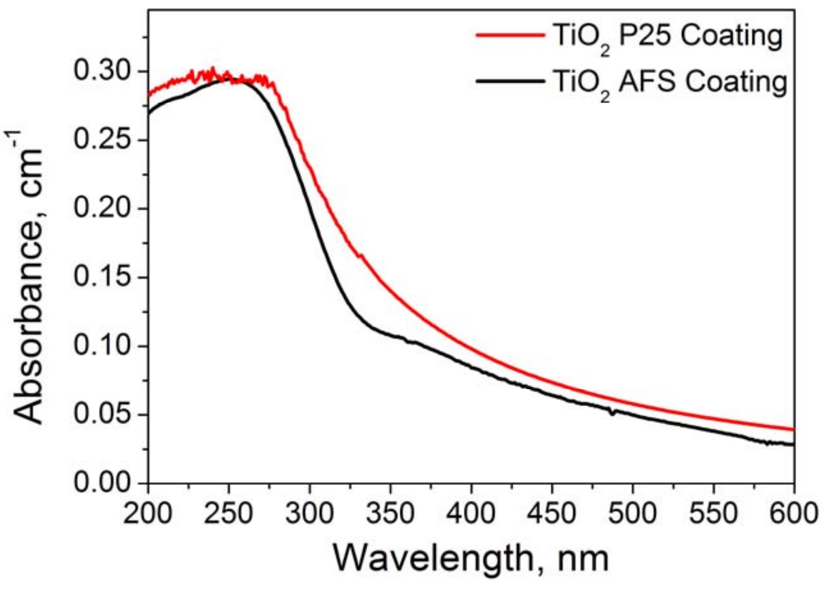

Figure 3: UV-Visible absorption spectra of P25 coating prepared by solvent evaporation technique and AFS TiO_2 coating obtained with a total deposition time of 30 s.

The antimicrobial activity of TiO_2 nanoparticle coatings was studied against the fungus *Candida Albicans*. The formation of *Candida Albicans* biofilm was investigated by staining with crystal violet (CV), which is able to colour the surface of the sample in purple. The reduction in the purple colour is directly related to the inhibition of biofilm formation. Once the biofilm is totally inhibited, a complete disappearance of the purple colour can be observed on the sample surface. The formation of fungus biofilm was evaluated both in the dark or under UV-light irradiation at λ=365 ± 1 nm for 2 minutes.

Figure 4 (left side) shows the quantification of *Candida* biofilm formation, using CV recovered with 200 µl of acetic acid. An uncoated aluminum substrate represents the positive control, on which *Candida Albicans* formed 100% of the biofilm. Compared to the control, the formation of biofilm on P25 coated substrates was almost unchanged, while on AFS TiO_2 coated sample was sensibly reduced down to 61%. So, it is possible to conclude that flame-synthesized titania coatings possess a high efficacy against *Candida Albicans* biofilm formation, while commercial P25 nanopowder did not demonstrate an equivalent efficacy. Figure 4 (right side) shows the results obtained under UV irradiation of the samples. The inhibition of biofilm formation on AFS titania coated substrate is enhanced by irradiation with UV radiation, resulting in an inhibition up to 90% of fungi adhesion on the sample surface. On the other hand, UV irradiation on P25 coating produced only a slight increase of the antifungal activity. Those findings can be related to both the higher amount of anatase in the phase composition of ASF TiO_2 compared to P25, and the increased exposed surface area due to the smaller dimension of nanoparticles forming the coating layer.

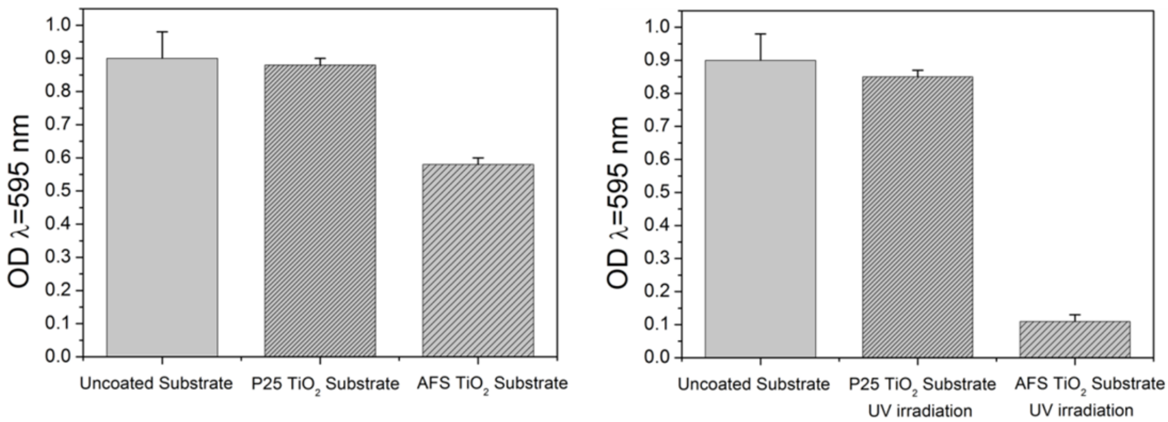

Figure 4: Biofilm mass quantification of CV stained cells on uncoated substrate, P25 coated substrate and AFS TiO_2 coated substrate with a total deposition time of 30 s (left); biofilm mass quantification of the same samples under UV irradiation conditions (right).

4. Conclusions

A new one-step method to produce tick coatings of flame-synthesized pure anatase TiO_2 nanoparticles on aluminium substrates by direct thermophoretic deposition was presented. A study of the antimicrobial efficiency was performed against the common indoor fungus *Candida Albicans*, and compared to commercial Aeroxide P25 nanoparticle coatings prepared by solvent evaporation technique. Flame-made coatings showed a higher antibacterial activity, due to their ability to protect the surface of the substrate against microbial biofilm formation, and a capability to enhance the antimicrobial activity under UV irradiation at a wavelength of 365 nm. The results obtained in this study are promising for using titania nanoparticle coatings as self-disinfecting material in both indoor and outdoor building materials that need a specific and continue sanitization.

References

Armelao, L., Barreca, D., Bottaro, G., Gasparotto, A., Maccato, C., Maragno, C., Tondello, E., Štangar, U. L., Bergant, M., Mahne, D., 2007, Photocatalytic and antibacterial activity of TiO_2 and Au/TiO_2 nanosystems, Nanotechnology, 18, 375709.

Balachandran U., Eror, N., 1982, Raman spectra of titanium dioxide, J. Solid State Chem., 42, 276–282.

Batchelor, G.K., Shen, C., 1985, Thermophoretic deposition of particles in gas flowing over cold surfaces, J. Colloid. Interface Sci., 107, 21–37.

Bellanger, A.P., Reboux, G., Roussel, S., Grenouillet, F., Didier-Scherer, E., Dalphin, J.C., Millon, L., 2009, Indoor fungal contamination of moisture-damaged and allergic patient housing analysed using real-time PCR, Lett. Appl. Microbiol., 49, 260-266.

Campoccia, D., Montanaro L., Arciola, C.R., 2013, A review of the biomaterials technologies for infection-resistant surfaces, Biomaterials, 34, 8533-8554.

De Falco G., Commodo M., Pedata P., Minutolo P., D’Anna A., 2016, Health issues concerning carbon-TiO_2 nanomaterials produced by flame synthesis, Chemical Engineering Transactions, 47, 439-444 DOI: 10.3303/CET1647074

De Falco G., Porta, A., Petrone, A.M., Del Gaudio, P., El Hassanin, A., Commodo M., Minutolo P., Squillace, A., D’Anna A., 2017, Antimicrobial activity of flame-synthesized nano-TiO_2 coatings, Environ. Sci.: Nano, 4, 1095-1107.

Kaeberlein, T., Lewis, K., Epstein, S.S., 2002, Isolating "uncultivable" microorganisms in pure culture in a simulated natural environment, Science, 296, 1127-1129.
Liberini, M., De Falco, G., Scherillo, F., Astarita, A., Commodo, M., Minutolo, P., D'Anna, A., Squillace A., 2016, Nano-TiO_2 coatings on aluminum surfaces by aerosol flame synthesis, Thin Solid Films, 609, 53–61.
Li, S., Ren, Y., Biswas, P., Tse, S. D., 2016, Flame aerosol synthesis of nanostructured materials and functional devices: Processing, modeling, and diagnostics, Prog. Energy Combust. Sci., 55, 1-59.
Liu, L., Zhao, H., Andino, J. M., Li, Y., 2012, Photocatalytic CO_2 Reduction with H_2O on TiO_2 Nanocrystals: Comparison of Anatase, Rutile, and Brookite Polymorphs and Exploration of Surface Chemistry, ACS Catal., 2, 1817–1828.
Madler, L., Roessler, A., Pratsinis, S. E., Sahmb, T., Gurlo, A., Barsan, N., Weimar, U., 2006, Direct formation of highly porous gas-sensing films by in situ thermophoretic deposition of flame-made Pt/SnO_2 nanoparticles, Sens. Actuators B, 114, 283–295.
Memarzadeh, S., Tolmachoff, E. D., Phares D. J., Wang, H., 2011, Properties of nanocrystalline TiO_2 synthesized in premixed flames stabilized on a rotating surface, Proc. Combust. Inst., 33, 1917-1924.
Nikraz, S., Phares, D. J., Wang, H., 2012, Mesoporous Titania Films Prepared by Flame Stabilized on a Rotating Surface: Application in Dye Sensitized Solar Cells, J. Phys. Chem. C., 116, 5342−5351.
Ruzmanova Y., Stoller M., Bravi M., Chianese A., 2015, A novel approach for the production of nitrogen doped TiO_2 nanoparticles, Chemical Engineering Transactions, 43, 721-726 DOI: 10.3303/CET15431.
Thimsen, E., Rastgar, N., Biswas, P., 2008, Nanostructured TiO_2 Films with Controlled Morphology Synthesized in a Single Step Process: Performance of Dye-Sensitized Solar Cells and Photo Watersplitting, J. Phys. Chem. C., 112, 4134–4140.
Verdier, T., Coutand, M., Bertron, A., Roques, C., 2014, A review of indoor microbial growth across building materials and sampling and analysis methods, Build. Environ., 80, 136-149.
Weir, A., Westerhoff, P., Fabricius, L., Hristovski, K., von Goetz, N., 2012, Titanium Dioxide Nanoparticles in Food and Personal Care Products, Environ. Sci. Technol., 46, 2242-2250.