CERAMIC NANOMATERIALS ON DIFFERENT MATRICES TOWARDS A HEALTHIER INDOOR ENVIRONMENT

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Introduction

Clean air is of vital importance to human health. Our challenge should be to provide the best of the outdoor environment, indoors. It is therefore a key factor in the overall quality of our life, to improve and maintain good air quality both outdoors and, in particular, indoors. Europe's building stock consists of >25 billion m^2 of buildings space of which >60% is more than 25 years old[1]. As our buildings are an economic asset and also represent a substantial environmental investment, it is our responsibility to minimise the resources used in the construction and refurbishment of buildings (primarily materials) and their operation (energy), a challenge that may be accomplished through the introduction of novel functional building envelope materials that can combine low cost with comfort and quality of life.

Photocatalytic material performances for indoor air cleaning

The daily average consumption of air by humans is 15-16 kg. At the same time in the industrialised nations, a person inhales 15-100 mg of poisonous carbon monoxide, formaldehyde, phenol, benzopyrene, *etc.* gases per day. Since 90% of our time we spend indoors, it is imperative to be surrounded by a clean and healthy environment. To this end, photocatalysis is considered an effective and economic solution. Photocatalytic (PC) materials have been shown to operate effectively in outdoor environments in reducing levels of harmful gases such as nitrous oxides and VOCs by stimulating their conversion to more benign products. In addition, they have shown to have deodourising, antifungal, anti-bacterial and self-cleaning functions[2-4]. The majority of these materials are based on titanium dioxide (TiO_2) as today's most active component while illuminated by ultraviolet light (UV). State of art active air purification systems using UV lamps have being developed for treating air of tunnel ventilators, underground parking places *etc.* Recently, a new generation of modified TiO_2 photocatalysts activated by diffused day-light and artificial light sources have been developed rending the material of utmost importance for indoor-air-quality (iAQ)

control while adopted for their potential as quiet, unobtrusive self-cleaning material additive to a number of useful matrices. The major interest from the side of the construction industry on these materials spins around the challenge to developing low cost functionalised building envelop materials with novel properties while maintaining critical components' properties. In this context combining materials introducing desired photocatalytic and or self-cleaning properties with conventional building envelope matrices such as paints or glass, wood, metal, cement surfaces may be the solution to effective low cost iAQ control.

In the present work, recent developments on the synthesis of patented modified TiO_2 effectively activated by low energy light sources are presented along with corresponding results on successful combinations with building materials tested either at lab or large scale projects. Facing the challenges of the indoor environment requirements we have developed a novel transition metal doped TiO_2 photocatalytic powder which operates across the range of indoor environmental conditions - temperature, humidity, illumination levels and spectrum (>420 nm)[6]. The material was also proved compatible with inorganic and selected organic coatings and colour paints used in interior and exterior surface areas (ceramics, paints, lime, cement, mortar, *etc.*) and the results were obtained when added to the appropriate matrix coatings at 5, 10% (Fig.1). In a more recent work, the Mn-doped TiO_2 was applied on

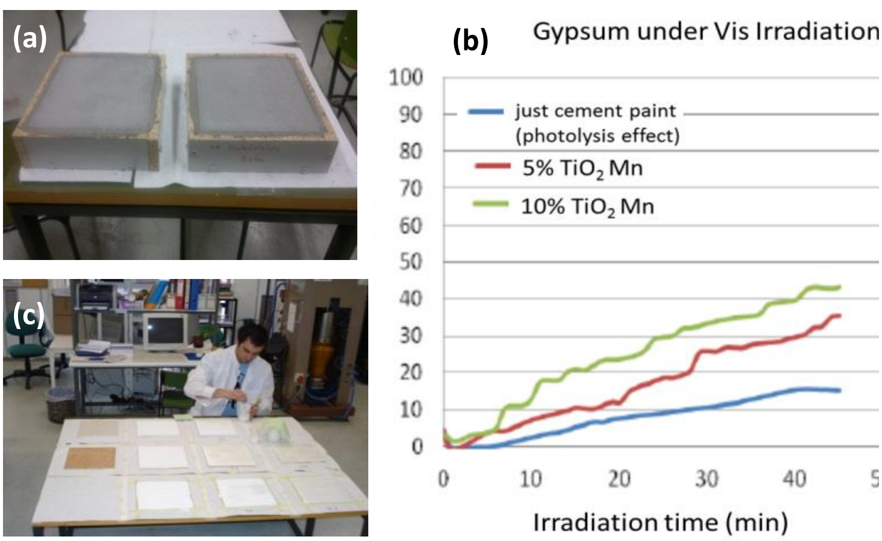

Figure 1: a, b) Cementitious coatings and responses of 5 & 10% PC material, c) Application of PC on plywood, gypsum and glass

substrates made of Fe-rich inorganic polymer mortars. For the synthesis, a slag originating from the gas plasma vitrification of landfilled mined residues was employed. The slag was almost completely amorphous, >98 wt%, as measured by QXRD and has a chemical composition in wt% of 37 SiO_2, 23 FeO, 21 CaO and 14 Al_2O_3. It was milled with an attritor mill until a Blaine surface of approx. 4000 cm^2/g and was subsequently mixed with two different K-silicate solutions, as presented in Table 1.

The inorganic polymer mortars were made by mixing the paste with standard CEN sand for one minute, at a slag/CEN sand mass ratio of 0.41. Afterwards the mortars were cast in cylindrical moulds of 20 cm high and a diameter of 6 cm and placed on a vibrating table for 1 minute, to release any residual air bubbles. The samples were cured in the moulds for 3 days at 22°C in a climate chamber and after demoulding open cured at ambient conditions in the lab for 4 months. The samples were subsequently coated with an optimum Mn-doped TiO_2 added at 5% w/w of a calcareous matrix coating, applied on the surface of two different Fe rich glass substrates. Consequently, they were analysed by the Environmental Research Laboratory (EREL) of the National Center for Scientific Research "DEMOKRITOS" in Athens, Greece in order to evaluate the photocatalytic efficiency of two of the coated Fe rich glass samples namely mortar 60M and 80M in reference to their corresponding uncoated counterpart. Analyses were performed in a certified test chamber following the CEN/TS 16980 "Continuous flow test method" standard. The photocatalytic abatement rate η (total) was calculated as the ratio of the difference between the NO concentration at the point of entry and the point of exit, following light exposure from the test chamber, over the value of the NO concentration at the point of entry. Following the above procedure, the intrinsic photocatalytic abatement rate was recorded as an intrinsic property of the material under test and thus it was possible to distinguish the photocatalytic activities of test samples with an absolute scale and with defined physical and engineering meaning (Table 1). The mortar produced with the activating solution containing the highest water content (80M) displays the largest NO (%) photocatalytic abatement rate. This effect can be attributed to the material porosity differences as the inorganic polymer paste in 60M and 80M have a BET N_2-adsorption surface of respectively, 6 m²/g and 40 m²/g.

In an effort to demonstrate the practical applicability and effective operation in a large scale projects, the Mn:TiO_2 photocatalytic material was incorporating into an inorganic paint plaster at a concentration rate of 8%. The resulted paint was used to cover the walls of a 400 m road tunnel (total surface of 4000 m^2) in Crete, in a joint venture with the Region of Crete has led to significant energy savings corresponding to more than 52 K Euros / year for the Region.

Table 1: The activating solutions in order to create a mortar or paste under PC test

Activating solution (AS)			Mortar composition				NO(%) photocatalytic abatement rate η(total)
H_2O in solution (wt%)	H_2O/K_2O (molar)	SiO_2/K_2O (molar)	Mortar code	AS/Slag (m/m)	AS/Slag (V/V)	Slag/ CEN sand	Blank / Coated
60	15.9	1.6	60M	0.44	0.91	0.41	0 / 22.63
80	42.3	1.6	80M	0.37	0.91	0.41	0 / 59.08

Conclusions

An account on the problem of air quality control has been presented based on solutions provided by modified TiO_2 materials, utilising the Photo-Catalytic oxidation process as an effective way to tackle the air pollution problem indoors. The successful synthesis of the photocatalytic material in powder form was verified by activation under UV and particularly under Vis light exposure rendering it as a promising material for indoor depollution applications. The photocatalytic material was successfully incorporated into cementitious matrices and was applied on different substrates such as plywood, gypsum and glass exposed to a range of inorganic (NO, NOx) and organic pollutants (VOCs, BTXs). In addition, independent tests on inorganic polymer matrices (made from Fe-rich slag) with varying pore structure, utilising the CEN/TS 16980 standard, were performed demonstrating the role of porosity of the substrate material on the overall photocatalytic performance of the coated samples. These promising results underline the compatibility between substrate and coating and open the way for a new range of functional building materials. Finally, a large-scale application has been reported where the photocatalytic materials employed have demonstrated both durability and effectiveness to tunnel clean air along with significant energy savings.

References

1. K. Koistinen *et al.*, INDEX project, "Critical Appraisal of the Setting and Implementation of Indoor Exposure Limits in the EU", 2005 EUR 21590 EN.
2. C. W. Lou, C. T. Lu, C. W. Lin, A. P. Chen, S. B. Jang and J. H. Lin, "Manufacturing Technique and Deodorization Effectiveness against Ammonia Gas of Bamboo Charcoal/Spandex Complex Knitted Fabrics", *J Eng Fiber Fabr*, **7** (2) 109-117 (2012).
3. S. B. Vučetić, O. L. J. Rudić, S. L. Markov, O. J. Bera, A. M. Vidaković, A. S. Skapin and J. G. Ranogajec, "Antifungal efficiency assessment of the TiO2 coating on façade paints", *Environ Sci Pollut Res Int*, **21** (19) 11228-37 (2014).
4. V. Roméas, P. Pichat, C. Guillard, T. Chopin and C. Lehaut, "Testing the Efficacy and the Potential Effect on Indoor Air Quality of a Transparent Self-Cleaning TiO2-Coated Glass through the Degradation of a Fluoranthene Layer", *Ind Eng Chem Res*, **38** (10) 3878–3885 (1999).
5. V. D. Binas, K. Sambani, T. Maggos, A. Katsanaki and G. Kiriakidis, "Synthesis and photocatalytic activity of Mn-doped TiO_2 nanostructured powders under UV and visible light", *Appl Catal B-Environ*, **113-114** 79-86 (2012).
6. C. Cacho, O. Geiss, J. Barrero-Moreno, V. D. Binas, G. Kiriakidis, L. Botalico and D. Kotzias, "Studies on photo-induced NO removal by Mn-doped TiO2 under indoor-like illumination conditions", *J Photoch Photobio A*, **222** 304– 306 (2011).