Characterization and Photocatalytic Activity of TiO_2 Nanoparticles on Modica and Comiso Stones

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Abstract

We report the results of a study on a new self-cleaning coating for limestone materials based on TiO_2 nanoparticles obtained by sol-gel. Structural and morphological characterization (AFM, SEM-EDS, Raman and UV-Vis techniques) indicate the crystalline anatase nature of the titania nanoparticles and confirm their photocatalytic activity. Tests on water vapor permeability, water absorption by capillarity, resistance to crystallization of salts and the measurement of the colorimetric parameters prove the chemical harmfulness of the coatings.

Introduction

Most historic buildings are located in urban areas and their condition has considerably got worse in this century, due to the synergistic action of natural weathering and of high concentrations of air pollutants. The main decay forms on the stone facades are related to soiling processes, with the development of black crusts in some specific areas. The main degradation causes are the urban environment and the water penetration through the stone surface.

Photoactive nanocrystalline titania by soft chemistry, i.e. sol-gel process not requiring additional thermal treatment, is a promising de-soiling and de-polluting coating material[1].

Materials & Methods

Two types of limestone among the most frequently used in Sicily were used as substrates: the Modica and Comiso calcarenite, of the "Ragusa Formation". The nano-TiO_2 sol was applied by brush coating directly to the stones or over a preliminary sol-gel SiO_2 based coating. The compatibility of the coatings with the stone substrate was investigated according to the UNI-Normal protocols[2-5] by measurements of water vapor permeability, water absorption by capillarity, resistance to salts crystallization and of colorimetric parameters.

The chemical, physical and structural characterizations were performed by means of petrographic polarized microscope, micro-Raman spectroscopy, AFM and SEM-EDS.

Photocatalytic oxidation of methyl orange dye (MeO), under fluorescent lamp irradiation, was used as a performance indicator of the catalytic activity of nano-TiO_2 sol. The effects of irradiation time and distance between the round-bottom flask containing the sol and the dye or and the light from the light source were also studied. The same study was performed on the coated stones.

Results and conclusions

Micro-Raman spectra confirm the crystalline nature of titania. The peak positions and the FWHM of the main peak[6] suggest anatase nanocrystals with size of 5-10 nm. A fast photocatalytic activity was measured both for TiO_2 sols (Fig.1) and for TiO_2 coatings. AFM images display a smoother surface

after the treatments. SEM-EDS analyses show different penetration depth for the investigated stones, depending on the type of stone and of the applied TiO_2 sol.

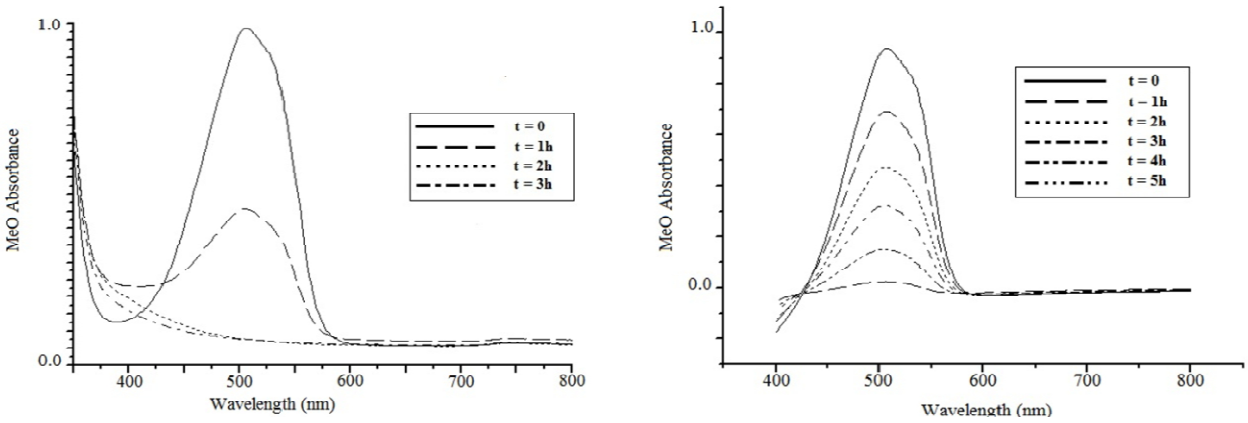

Fig.1 - Photodegradation profile of methyl orange (MeO) by nano-TiO_2 sol, at 10 cm (left) and 20 cm (right) from the UV lamp, as a function of time.

The TiO_2-based self-cleaning treatment introduces negligible colorimetric modification with respect to the untreated limestone and does not alter the properties of the stone as determined by measurements of water vapor permeability, water absorption by capillarity and resistance to salt crystallization. Raman analyses carried out after these tests show the presence of anatase, confirming the persistence of the TiO_2 coatings after the tests.

The sol-gel nanocrystalline TiO_2, applied directly to the stone or over a silica substrate, is a simple way to obtain photocatalytic de-soiling coatings without significantly changing the morphology and the chemical-physical properties of the Modica and Comiso limestones.

References

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