



Photocatalytic activity of ZnO and TiO₂ ‘nanoparticles’ for use in cement mixes

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HIGHLIGHTS

- TiO₂ and ZnO nanoparticles protected against fungal fouling of calciferous materials.
- Light exposure was not necessary for antifungal activity.
- ZnO was more effective than TiO₂.
- Commercial nanoparticle suspensions contained microparticles over 100 nm.

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ABSTRACT

Commercial titanium and zinc nanoparticle suspensions were tested for use in self-cleaning and protection of built cement structures. The methylene blue decolorization test, assessment of activity against the fungus *Cladosporium* sp. in laboratory cultures, and accelerated testing for anti-fungal activity on gypsum panels all showed that the Zn particles were more effective than TiO₂ (both at 4%). The commercial “nanoparticle” suspensions were shown, by scanning electron microscopy and electron dispersive spectroscopy, to have a size range outside that required for classification as nanoparticles and should more correctly be characterized as microparticles. The large surface area of these particles, together with their obvious photocatalytic activity shown by the methylene blue test, as well as their apparent inherent antimicrobial activity, indicate that the ZnO particle suspension is more effective and appropriate for inhibition of fungal growth on calciferous building materials than the more commonly used TiO₂.

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1. Introduction

Increasing temperatures in the World's urban centres has led to the development of new products for improving thermal comfort within buildings. The envelopes of buildings play a fundamental role in the production of heat islands in large cities. Various strategies have been used to minimize this problem, one of which is the employment of building surfaces with higher solar radiation reflectance. In general, light coloured coatings have higher reflectance than dark. However, it is not only the colour that influences absorption of radiation, but also the chemical and mineralogical composition of the material. Hence it is possible to produce darker coloured coatings with high reflectance [1,2].

The appearance of white and coloured façades changes on exposure to the environment. Apart from natural degradation,

deposition of biological organisms and atmospheric pollutants such as fuel emissions alters the optical and thermal properties of external coatings (see Fig. 1).

Discoloration by microbial deposits (biofilms) is particularly important in hot and humid environments. The types of microorganisms and the rate at which they colonise a surface will depend not only on relative humidity and temperature, but also on exposure to the sun (insolation) and microclimate [3]. Antimicrobial substances are often incorporated into surfaces to avoid or reduce this effect.

Nanoparticles of TiO₂ (n-TiO₂) have been used for some time to produce surfaces that are self-cleaning on exposure to light through photocatalytic destruction of organic materials; the best studied treatments combine this activity with water repellence [4]. Current treatments are based on a mixture of silane/siloxane hybrids with TiO₂ nanoparticles, which reduce both urban chemical pollution and biological colonization on the surface. Apart from maintaining initial reflectance and emission of solar radiation, the aesthetics of the building are also retained. Silver nanoparticles

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Fig. 1. São Paulo façades discolored by biological colonization (patterned grey staining).

(n-Ag) have been shown to act against microbial cells by penetrating the cells and interfering with membrane proteins [5]. After entering eucaryotic cells, they cause mitochondrial dysfunction, resulting in an increase of reactive oxygen species (ROS). ROS cause oxidative stress, damaging proteins and nucleic acids [6]. Zinc and titanium nanoparticles act in the same fashion against fungi and algae, the major organisms involved in discoloring biofilms on building façades [7].

Nanoparticles of SiO_2 have been used to improve the tensile strength of mortars [8], but other nanometals which can improve resistance to discoloration of cementitious materials have scarcely been studied. Oxides of zinc and titanium of micrometer size have similar light-interacting properties – refraction, dispersion, reflection and diffraction – and could be efficacious in this respect. Although ZnO is less efficient in these interactions, it has the advantage of being much more versatile, with wider application than TiO_2 [9]. As nanostructures, the two oxides are also similar, but n-ZnO has lower photodegradation efficiency. Both oxides are white, are wide range semiconductors, slightly soluble in water and much used in photocatalytic processes, but neither has been substantially employed on building surfaces [10], although TiO_2 has been investigated, with disappointing results, for the removal of diesel exhaust soot from mortar [11]. The only reports found in the literature on use of ZnO nanoparticles in buildings are those of the Portsmouth group published in 2012 [12–14]. They studied application on tiles, mortar and façades with the aim of improving thermal insulation and energy economy.

Here, we report a laboratory scale comparison between titanium and zinc commercial nanoparticle suspensions for use in self-cleaning and protection of cement façades.

2. Materials and methods

The test cementitious material was 1:1 (w/w) white cement coating and calcareous filler (Art Spray – Texturas Especiais, Jandira, São Paulo, Brazil).

Nanomaterials used were:

- 80–200 nm particles of n-ZnO from Research Nanomaterials, Inc., Houston, Tx, USA;
- n- TiO_2 P 25 (Evonik, São Paulo, Brazil).

Photocatalytic activity of the nanoparticle suspensions was checked by the methylene blue decolorization test [15]. Four concentrations of n-ZnO and n- TiO_2 (0.5%, 1.0%, 1.5% and 3.0%) were prepared in 100 mL 0.03 g/L aqueous methylene blue and in methylene blue saturated with calcium hydroxide, to mimic the alkalinity of newly produced cement. Tubes were exposed to UV irradiation for 9 h in a chamber containing a Phillips HPL-N lamp and high-pressure mercury bulb. The glass casing was removed from the lamp so as not to interfere with the UV radiation. The

reduction in blue coloration caused by oxidation of the dye was assessed visually.

For microscopic analysis, nanoparticles were mixed with the cement-based coating at 4%, this concentration being based on the results reported in Dantas et al. [16]. After sputter coating with platinum, they were analysed by scanning electron microscopy (SEM, FEI, model Quanta 600 FEG) and energy dispersive spectroscopy (EDS, Bruker, model Quantax 4030).

The inhibitory effect of n-ZnO and n- TiO_2 on the fungus *Cladosporium*, isolated from painted coupons exposed in the campus of USP, São Paulo, especially for this project, was evaluated by standard microbiological tests in petri dishes and by an accelerated laboratory test using gypsum panels. The fungal culture is available from the culture collection of Dr. Marcia Shirakawa at the Polytechnic School of USP.

For petri dish tests, a 72 h culture of *Cladosporium* sp. was suspended in 0.1% sterile glucose to give a final concentration of 10^7 spores/mL. Fifty μL of the nanoparticles (4%) were spread over Sabouraud Dextrose Agar, followed by 50 μL of the spore suspension. The plates were maintained in a climate chamber for 72 h, with or without exposure to light from a Phillips HPL-N 125 W lamp. Triplicate plates, with and without nanoparticles, were incubated at 25 °C for 72 h in an illuminated (fluorescent light) incubator and then examined with the naked eye to determine the amount of growth.

Accelerated analysis of antifungal activity was carried out using gypsum, rather than cement, as the substrate, in order to allow the growth of microorganisms without the need for carbonation. For the accelerated test, glass slides were coated with 9.6 g of gypsum (Usina Fortaleza, São Paulo, Brazil). One mL of 0.4 g/10 mL of either ZnO or TiO_2 nanoparticles was applied with a micropipette. When dry, one drop (50 μL) of a spore suspension of *Cladosporium* sp. (10^7 spores/mL in 0.1% glucose) was placed in the middle of the coated slide. After drying at 42 °C for 24 h, the slides were exposed to the following conditions: 1) natural solar irradiation (on 24/02/2016, from 12noon to 1:45 pm, in the campus of USP, São Paulo, Brazil), 2) a Phillips HPL-N 125 W lamp, 3) darkness produced by covering with aluminium foil. Slides were then incubated in a humid chamber (Bass Equipamentos, São Paulo, Brazil) at $25 \pm 3^\circ\text{C}$ for 14 days, with alternating cycles of 12 h light (Phillips lamp model ST8-HB2 9 W/830 600 mm) and 12 h dark. They were then examined using a petrographic (reflected light) microscope (Leica, model DM750P) and by digital microscopy, using a Hirox microscope (KH7700 with MXG-2500REZ lens).

3. Results

The methylene blue decolorization test showed that, under all conditions, n-ZnO of particle size 80–200 nm (as stated by the manufacturer) caused complete decoloration after 9 h, with n- TiO_2 P 25 producing high, but not complete, decoloration.

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