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Preventing fungal growth in wood by titanium dioxide nanoparticles

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ABSTRACT

Fungi play a considerable role in the deterioration of cultural heritage, as their contamination favours the decay of the materials used for historical art objects. Fungus prevention, the treatment of contaminated objects and their successive conservation are important items to restorers. Over the past decade, nanotechnology has been applied in several fields of cultural heritage conservation in order to prevent, for example, the chemical degradation of mural paintings and paper acidity. Nevertheless, nanomaterials have not been yet used as antifungal and biocidal agents for wood handworks. In this work we have treated eight different types of wood, some of which are commonly used in the field of cultural heritage, with a solution of titanium dioxide nanoparticles and placed them in contact with two species of fungi, *Hypocrea lixii* (white-rot) and *Mucor circinelloides* (brown-rot), which are known to be responsible for a fast decay of wood. Results show that the photo-catalytic activity of titanium dioxide nanoparticles prevents the fungal colonization of wood samples over long time when compared to untreated ones.

1. Introduction

The term *nano* refers to materials whose dimensions are less than 100 nm. Nanomaterials are characterized by a high surface/volume ratio, which gives them larger activities in surface related phenomena (e.g. adsorption, reaction rates, electronic conductivity, etc.) compared to bulky systems with same mass (De Filpo et al., 2006, 2010). Particular environmental remediation applications are based on redox reactions from semiconductors, especially titanium dioxide, which photo-catalytically degrade organic compounds into harmless inorganic compounds (Herrmann, 1999; Nicoletta et al., 2012). When a semiconductor catalyst, e.g. titanium dioxide, in contact with water and oxygen molecules adsorbs some radiation with an intensity of energy that is larger than the characteristic band-gap, electrons are promoted from valence band to conduction band, creating free electrons and electron holes pairs ($e^-_{cb} + h^+_{vb}$) (Hoffmann et al., 1995; Minero, 1995; Rauf et al., 2007). Both electrons and holes can move to the semiconductor surface and produce reactive oxygen species like superoxide anions and hydroxyl radicals, which can oxidize organic compounds, whereas electrons can reduce them (Mahmoodi et al., 2006), as sketched in the following reactions:

$$TiO_2 + h\nu \rightarrow e^-_{cb} + h^+_{vb}$$
$$O_2 + e^-_{cb} \rightarrow O_2^{-\bullet}$$
$$H_2O + h^+_{vb} \rightarrow OH^\bullet + H^+$$
$$O_2^{-\bullet} + H_2O \rightarrow H_2O_2 \rightarrow 2OH^\bullet$$
$$OH^\bullet + OC \rightarrow OC_{ox}$$
$$OC + e^-_{cb} \rightarrow OC_{red}$$

A lot of research has been recently devoted to the modification of semiconductor band-gap in order to shift their photo-activity to the visible region (Han et al., 2009). In particular, semiconductors have been modified by doping with noble metals (e.g. Au, Ag, and Pt), transition elements (such as Fe^{3+}, Mo^{5+}, Ru^{3+}, V^{+4}, Rh^{3+}), lanthanides (including Eu, Ce, Nd, Er, Pr, Sm, and La), alkaline metals (such as Li, K, and Na), CdS, non-metals (e.g. N, F, S, B, and C), and dyes (Asahi et al., 2001; Yu et al., 2005; Wong et al., 2006; Hu et al., 2007; Lan et al., 2007; Li et al., 2007; Kubacka et al., 2009).

Titanium dioxide is a semiconductor with a band-gap of 3.2 eV (absorption wavelength less than 380 nm) characterized by long term stability, and UV photo-activity (Keller et al., 2010). In addition to the mineralization of organic compounds, this last property ensures to TiO_2 nanoparticles/films antibacterial and antifungal abilities due to the production of reactive redox species. In fact, the TiO_2-generated hydroxyl radicals ($OH^\bullet$), superoxide anions ($O_2^{-\bullet}$), and hydrogen peroxide molecules (H_2O_2) damage cell membrane (Cho et al., 2004) and can inactivate a wide range of organisms

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Fig. 1. Wood biodeterioration from white- (on the left) and brown-rot (on the right) attack.

(Huang et al., 2000) (bacteria, viruses, fungi, and algae). Consequently, photocatalysis has been suggested as an alternative technique for surface sterilization and water purification (Fujishima et al., 2000). Since the early works of Matsunaga et al. (1985, 1988) on the inactivation of *Escherichia coli*, several authors have reported the biocidal properties (disinfection) of pure titanium dioxide upon UV light irradiation (Matsunaga and Okochi, 1995; Koizumi and Taya, 2002). Such biocidal activity can be enhanced by co-doping nanoparticles with silver, carbon, and sulphur (Hamal et al., 2010).

Environmental pollution can cause deterioration of stone materials and favour biological attacks by microorganisms. The biological decay of cultural heritage buildings is a serious problem considering the cleaning and repairing costs and, eventually, the cultural losses (Chen and Blume, 2002). Following the works on construction and building materials (Chen and Poon, 2009; Maury Ramirez et al., 2010), Fonseca et al. (2010) have recently proposed, for the first time, an alternative application of titanium dioxide for preventing bio-deterioration of mortars in cultural heritage buildings. Both *in lab*- and *in situ*- (Palácio Nacional da Pena, Sintra, Portugal) treatments showed the biocidal and preventing bio-deterioration properties of titanium dioxide (pure and Fe^{3+}-doped anatase form) against lichens and other phototropic microorganisms. Furthermore, the TiO_2 treatments resulted to be more effective than other conventional biocides, which, generally, suffer from short term protection and toxicity towards environment and health (Chen et al., 2009; Shabir Mahr et al., 2013). Nevertheless, it should be mentioned that a risk assessment for TiO_2 nanoparticles has not been published yet even if they are a common additive in many foods and personal care products (Weir et al., 2012).

Table 1
Wood types tested in this work and their number id (# 1–8). Fungal resistance score: 1, very durable; 2, durable; 3, moderately durable; 4, not very durable; 5, non-durable. Data on line at http://www.sfera-group.it.

Wood id	Wood type	Binomial name	Rot fungal resistance
1	Scots pine	*Pinus sylvestris* L.	3–4
2	Silver fir	*Abies alba M.*	4
3	Walnut	*Junglas regia* L.	3
4	Chestnut	*Castanea sativa M.*	2
5	Wild cherry	*Prunus avium* L.	1
6	Sessile oak	*Quercus petrea* L.	2
7	Beech	*Fagus sylvatica* L.	5
8	Ash	*Fraxinus excelsior* L.	5

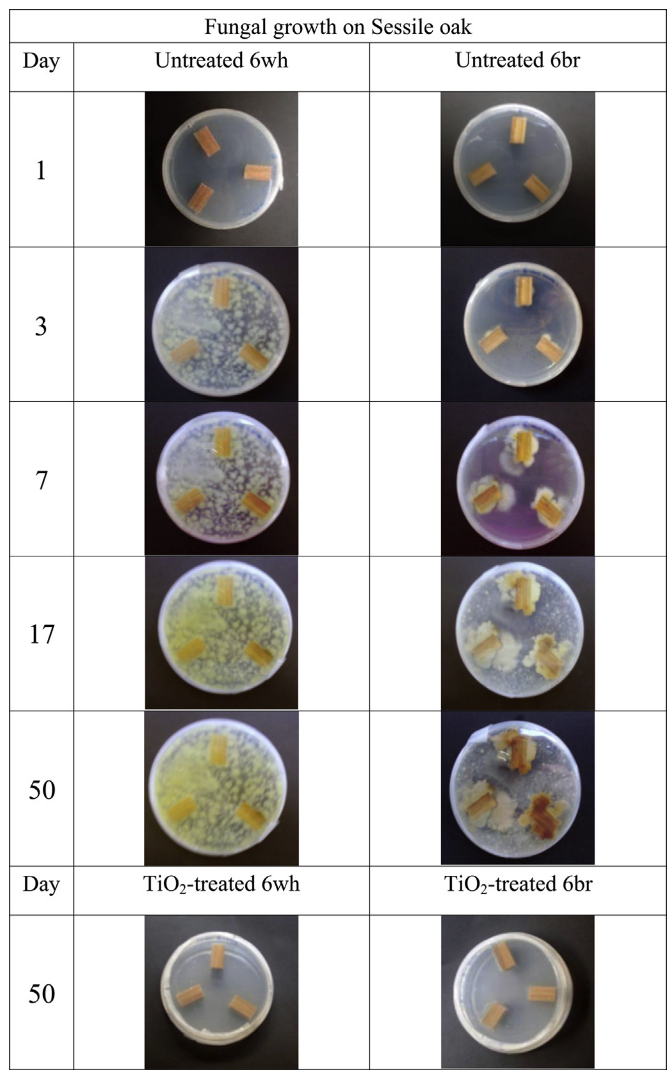

Fig. 2. Fungal growth on untreated and TiO_2-treated Sessile oak samples. 6wh and 6br id stands for Sessile oak sample contaminated by white- and brown-rot fungi, respectively. The two last pictures are referred to TiO_2-treated Sessile oak samples after fifty day from white- and brown-rot fungi inoculation. No fungal attack is evident in both cases.