



A designed UV–vis light curable coating nanocomposite based on colloidal TiO₂ NRs in a hybrid resin for stone protection

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ABSTRACT

The modification of a UV–vis light curable hybrid methacrylic–siloxane resin with organic coated TiO₂ nanorods (NRs) has been carried out, in order to fabricate a functional coating for protection of stone artefacts of artistic and cultural relevance. The nanocomposite, formulated without using any harmful and high volatile monomer components, has been deposited onto the surface of stone samples made of a porous carbonate stone, namely Lecce stone. Such a building material, specifically selected as a relevant example of porous and light coloured stone, is widely used in monuments and constructions of cultural and historic interest of the Apulia region (Italy). The protective ability of the nanocomposite against the water vapour capillarity absorption and its self-cleaning properties have been investigated as a function of the TiO₂ NR loading, the applied amount of the formulation and the curing conditions. A reliable protocol for the application of the nanocomposite has been implemented, and, remarkably, a single UV–vis light curing step has resulted in a uniform and hydrophobic coating layer, able to preserve the water vapour permeability, the pristine colour and surface morphology of the stone samples. Moreover, the nanocomposite coated stone surface has demonstrated self-cleaning ability when tested for the degradation of an organic molecule, used as a model compound, under both solar light simulated and real sun irradiation. The achieved nanocomposite has ultimately proven to be technologically advantageous as a functional coating, suited to protect surfaces of artistic, archaeological monuments of historical interest, also under outdoor conditions.

1. Introduction

Stone monuments, bas-reliefs and artistic artefacts are subjected to physical-chemical weathering due to rain and moisture, temperature excursions, mechanical stress and environmental pollution. Water penetration into pores by capillarity causes (bio)deterioration, reactions with acid rains and micro-organism actions. The application of hydrophobic and self-cleaning coatings, based on photocatalytically active inorganic nanoparticles (NPs), dispersed in hydrophobic resin formulations, can be considered a suitable strategy to limit the (bio)deterioration of valuable pieces of Cultural Heritage.

TiO₂ in nanocrystalline form is widely used in exterior and interior construction furnishing materials, due to its low toxicity, commercial availability, optical transparency in the visible spectral range, photo and chemical stability and excellent antimicrobial and photocatalytic activity [1]. TiO₂ NP based coatings, achieved by dispersing

commercial TiO₂ P25 NPs in water, have been applied on marble surfaces to prevent bacterial activity [2,3], while hydrolytically pre-synthesized TiO₂ NPs dispersed in water, or TiO₂ NPs synthesized from titanium alkoxides through sol-gel process and then hydrothermal crystallization [4], have been applied as protective materials on travertine [5,6]. This type of coatings typically suffers for a limited photocatalytic efficiency, caused by NP aggregation and formation of inhomogeneous and cracked films, causing detachment of the photocatalyst from the supporting surface.

The integration of colloidal nanosized TiO₂ photocatalyst in a polymer host should, in principle, overcome the problems related to catalyst aggregation and phase separation issues, leading to uniform and mechanically stable functional nanocomposites. Moreover, the polymer matrix in nanocomposites is expected to improve the hydrophobicity of the coating, finally resulting in a suitable protective material.

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The design of a performing and convenient photocatalytically active nanocomposite has, however, to cope with the inherent limitation arising from the ability of the embedded NPs to degrade the organic host matrix [7]. In fact, acrylic polymers, polyethylene, polyurethane, polystyrene and vinyl based polymers, embedding pre-synthesized TiO₂ NPs, when manufactured into photocatalytic and antimicrobial self-cleaning coatings, have shown the tendency to be degraded by the TiO₂ NPs itself [8]. In addition, these coatings are based on monomers that require a thermal curing process, up to several weeks long, to completely polymerize on the stone in outdoor conditions, and, therefore, the final properties of the coating result strongly affected by the surrounding environmental conditions [9].

A host matrix based on an inorganic-organic sol-gel hybrid material has demonstrated to withstand the risk of the photocatalytic degradation, since the inorganic network protects the organic part [10,11]. Sol-gel hybrid materials have been successfully applied in several industrial fields. Some examples are in ophthalmic market to improve scratch and abrasion-resistance of contact lens surfaces, in painting industry as corrosion-resistant primers and as high-temperature coatings for steel, in glass packing industry for colouring and improving the mechanical properties of glass bottles and in automotive sector, for providing colouration, but also scratch-resistance and protection from UV and chemical attack [12].

Recently, a mesoporous titania-silica composite, formulated by mixing ethoxysilane oligomers with commercial TiO₂ P25 NPs and the *n*-octylamine surfactant, has been prepared [13,14] by an inverse micelle mechanism [15], as a self-cleaning, hydrophobic, consolidant, adhesive and crack-free mesoporous coating for concrete and stones.

In this work, a purposely designed solvent-free, UV–vis light photopolymerizable nanocomposite material made of a hybrid methacrylic-siloxane resin, modified with 1 wt% of oleic acid (OLEA) and 3-(trimethoxysilyl)propylmethacrylate silane (OLEA/MEMO)-coated TiO₂ nanorods (NRs), has been tested as a protective coating for Lecce stone, a carbonate stone, used in historic monuments and buildings of the Apulia region (Italy), and specifically selected in this study, for its porosity and aesthetical properties.

Recently, dispersions of OLEA-capped TiO₂ NRs, have resulted effective in self-cleaning and protecting the Lecce stone [16]. Here, OLEA-coated TiO₂ NRs have been synthesized in anatase phase, by means of an established colloidal route able to provide NRs with an accurate control on size, shape and crystalline quality [17]. Nanocrystals with a pronounced anisotropy in shape have been selected because of their enhanced photoactivity [18]. Indeed, after light excitation, the e⁻ and h⁺ photogenerated in the anisotropic nanostructure can be more effectively delocalized along the longitudinal direction, thus limiting the detrimental e⁻/h⁺ recombination, and resulting in an efficient generation of ROS (Reactive Oxygen Species) [18].

The preparation of the nanocomposite needs preliminary capping exchange procedures at the nano-objects surface to increase their compatibility with the methacrylic-siloxane resin formulation [19]. Major components of the hybrid methacrylic-siloxane resin are vinyl terminated polydimethylsiloxane (VT PDMS), trimethylolpropane trimethacrylate (TMPTMA) and trimethoxypropyl silane methacrylate (MEMO). Then, the silane coupling agent MEMO has been grafted at the NR surface. Namely, the –Si–O– network of VT PDMS and MEMO present high chemical compatibility with inorganic substrates, and hence convey to the formulation high adhesion to the stone surface. The –CH₃ groups of PDMS provide the resin hydrophobic character and the –C=C– moieties of TMPTMA, MEMO and VT PDMS provide the curing of the resin matrix. Such a resin formulation has demonstrated a high optical transparency, permeability to water vapour and excellent anti-fouling and weathering resistance [20]. The low molecular weight and the low viscosity of such a resin, along with an in-situ and rapid (few hours) UV–vis light induced polymerization, prevent detrimental plasticizing effects due to environmental conditions, and do not require any additional calcination step or solvent/surfactant extraction after

application on the substrate, thus resulting in highly amenable characteristics of such a resin formulation [21]. Indeed, these features contribute in achieving the resin penetration inside porous substrates, leading to uniform, completely cured and very adherent coatings [22], characterized by a glass transition temperature (T_g) higher than those achieved by means of thermal polymerization or by solution based processes [20–22].

2. Material and methods

2.1. Chemicals

Oleic acid (OLEA, 90%), titanium tetraisopropoxide (Ti(OⁱPr)₄ or TTIP, 98.9%) and trimethylamino-*N*-oxide dihydrate ((CH₃)₃NO·2H₂O or TMAO, 98%) were achieved from Fluka. Trimethoxypropyl silane methacrylate (MEMO) and trimethylolpropane trimethacrylate (TMPTMA) were purchased by Cray Valley. Vinyl terminated polydimethylsiloxane (VT PDMS) with an average molecular weight of 25,000 g mol⁻¹, 3-Mercaptotriethoxysilane (MPTS) and diethylamine were achieved from Aldrich. Bis(2,4,6-trimethylbenzoyl)-phenylphosphineoxide and 2-hydroxy-2-methyl-1-phenyl-1-propanone, named here Irgacure819 and Darocur1173, respectively were supplied by Ciba. TiO₂ Aeroxide from Evonik was used as a reference material to be dispersed in the resin formulation.

2.2. Stone samples

Stone samples were used in order to assess the protective effect of photopolymerizable nanocomposites based on the hybrid methacrylic-siloxane modified resin formulations loaded with the OLEA/MEMO-coated TiO₂ NRs. A building stone type, extracted in Salento area (Lecce, Italy) and known as Lecce stone (or *Pietra Leccese*), was selected as a significant example of porous carbonate stone, extensively used in historic monuments and buildings in the Apulia region (Italy).

2.3. Synthesis of oleic acid (OLEA)-coated TiO₂ Nanorods (NRs)

TiO₂ NRs, synthesized by a colloidal approach in presence of surfactants that induce at the surface a coordination layer of oleic acid (OLEA), were prepared with a diameter of 3–5 nm and length of ca. 20 nm under nitrogen atmosphere, as reported in [17].

A standard air-free technique for manipulating dried and degassed reactants was used. The synthesis was performed at 80–100 °C, by hydrolysis of the TTIP precursor in the OLEA surfactant, and in the presence of the aqueous TMAO base solution in excess, which catalyzes polycondensation of the precursor [17]. The OLEA-coated TiO₂ NRs were purified from the reaction mixture by using methanol as a non-solvent, and then dispersed in chloroform.

2.4. Ligand exchange of oleic acid capped TiO₂ NRs with 3-(trimethoxysilyl)propylmethacrylate (MEMO)

The pristine OLEA ligand molecules coordinating the TiO₂ NR surface were partially displaced with 3-(trimethoxysilyl)propylmethacrylate (MEMO), by following, with minor modifications, the route reported by De Palma et al. [23,19]. The removal of most of the OLEA ligand coordinating the TiO₂ NR surface, was carried out by purifying the NRs by several cycles of dispersion in ethanol, followed by isolation with centrifugation. Then, the NRs were dispersed in hexane and MEMO and acetic acid were added in a 1:10 TiO₂/MEMO and 1:3 MEMO/acetic acid molar ratio, respectively, and the solution was left to stir overnight. As a proof of the effective occurrence of the capping exchange, the solution turns from transparent to opaque under stirring, because of the aggregation of the OLEA/MEMO-capped TiO₂ NRs in hexane. Finally, the OLEA/MEMO-coated TiO₂ NRs were purified from the excess of MEMO and from the displaced OLEA, by two cycles of

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