



Assessing the effects of UVA photocatalysis on soot-coated TiO₂-containing mortars

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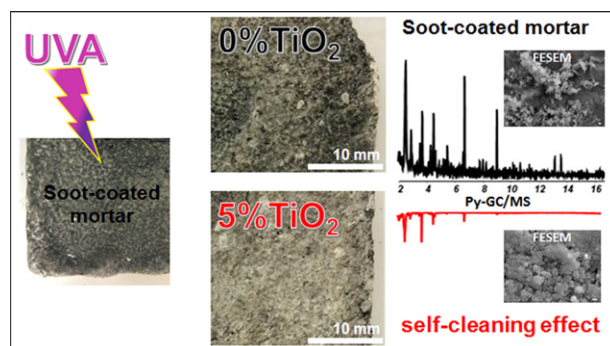
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HIGHLIGHTS

- Lime mortars were prepared with TiO₂ and coated with diesel soot deposits.
- Colour measurements and SEM revealed self-cleaning effect after 30 days of UVA exposure.
- Py-GC/MS showed the cracking of PAHs and *n*-alkyl compounds of the soot after UVA irradiation.
- Solid-state ¹³C NMR was a reliable analytical technique for the evaluation of soot photo-oxidation.
- ¹³C NMR spectroscopy demonstrated chemical changes on the soot organic constituents.

GRAPHICAL ABSTRACT



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ABSTRACT

The deposition of soot on building surfaces darkens their colour and leads to undesirable black crusts, which are one of the most serious problems on the conservation of built cultural heritage. As a preventive strategy, self-cleaning systems based on the use of titanium dioxide (TiO₂) coatings have been employed on building materials for degrading organic compounds deposited on building surfaces, improving their durability and performance. In this study, the self-cleaning effect of TiO₂-containing mortars coated with diesel soot has been appraised under laboratory conditions. The mortar samples were manufactured using lime putty and two different doses of TiO₂ (2.5% and 5%). The lime mortars were then coated with diesel engine soot and irradiated with ultraviolet A (UVA) illumination for 30 days. The photocatalytic efficiency was evaluated by visual inspection, field emission scanning electron microscopy (FESEM) and colour spectrophotometry. Changes in the chemical composition of the soot particles (including persistent organic pollutants) were assessed by analytical pyrolysis (Py-GC/MS) and solid state ¹³C NMR spectroscopy.

The FESEM and colour spectrophotometry revealed that the soot-coated TiO₂-containing mortars promoted a self-cleaning effect after UVA irradiation. The combination of analytical pyrolysis and ¹³C solid state NMR showed that the UVA irradiation caused the cracking of polycyclic aromatic structures and *n*-alkyl compounds of the diesel soot and its transformation into methyl polymers. Our findings also revealed that the inclusion of TiO₂ in the lime mortar formulations catalysed these transformations promoting the self-cleaning of the soot-stained

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mortars. The combined action of TiO₂ and UVA irradiation is a promising proxy to clean lime mortars affected by soot deposition.

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1. Introduction

In urban environments, the deposition of air pollutants and organic particulate matter (soot particles, polycyclic aromatic hydrocarbons, sulphur compounds, spores) is responsible for the formation of black crusts on building envelope surfaces (Hermosin et al., 2004; Montaña et al., 2008; Papida et al., 2000). Nowadays, these crusts represent one of the most important deterioration forms on the European built heritage with significant aesthetic, economic and cultural implications (ICOMOS, 2008; Pozo-Antonio et al., 2016; Rivas et al., 2014; Sleiman et al., 2014, 2015). This has prompted the seeking of novel engineering and conservation strategies to reduce soot deposition on cultural heritage assets (Karatasios et al., 2010; Ruot et al., 2009).

Soot particles are produced during incomplete combustion processes, such as car engines, industries, domestic heating systems or forest fires, from volatile precursor compounds formed during pyrolysis that subsequently release carbon-rich particles (Schmidt and Noack, 2000). This pyrogenic organic material is omnipresent in the atmosphere, soils, sediments, ice and building surfaces due to its widespread emission in most industrial cities and high stability in the environment (Goldberg, 1985). Other persistent organic pollutants are the polycyclic aromatic hydrocarbons (PAHs), which are occluded in the soot matrix during the incomplete combustion process (De la Rosa et al., 2016). Despite soot particles were traditionally considered relatively unreactive, this pyrogenic organic matter can indeed be degraded (De la Rosa and Knicker, 2011). Kim et al. (2013) showed that soot-associated PAHs can be degraded by photolysis. Energetic UV photons have sufficient energy to disrupt chemical bonds in many materials including soot particles. The absorption of UV energy can cause the breaking and/or crosslinking of polymeric compounds, leading to altered chemical and mechanical properties of the polymers. After disruption of the initial chemical state, the polymers are likely to react with oxygen and/or water vapour causing additional changes. Another type of photo-degradation can occur due to photo-absorption by inorganic pigment particles such as titanium dioxide (TiO₂). An electron–hole pair is formed in the pigment particle. A photo-excited hole can then migrate to the particle's surface and cause a deleterious chemical reaction in the polymer (Kim et al., 2013). For this reason, white TiO₂ nanoparticles are usually tested as thin coatings on building surfaces to mitigate biological colonization and fuel soot deposition on mortars (Bengtsson and Castellote, 2014; Diamanti et al., 2008; Fonseca et al., 2010; Munafò et al., 2015; Paolini et al., 2016; Pinho et al., 2013; Quagliarini et al., 2012; Senff et al., 2013; Smits et al., 2013). Anatase is one of the most common crystalline forms of TiO₂ and is characterised by its great photocatalysis, which is the acceleration of a photochemical reaction by means of a catalyst interacting with light of sufficient energy (Lucas et al., 2013; Toma et al., 2004). The photocatalytic reaction takes place on the surface of the building materials where the adsorption of the gaseous pollutants occurs (Fujishima et al., 2008). Despite carbon photo-oxidation has been previously reported (Kim et al., 2013), the chemical changes experimented by soot-derived organic compounds are not well understood.

This study assessed the photocatalytic degradation of diesel soot particles deposited on lime-based mortars containing TiO₂ nanoparticles after 30 days of UVA irradiation. For these purposes, visual examination, field emission scanning electron microscopy (FESEM), colour spectrophotometry, solid state ¹³C nuclear magnetic resonance (NMR) spectroscopy and pyrolysis coupled with gas chromatography/mass spectrometry (analytical pyrolysis) were applied.

Several authors have determined the photocatalytic action of TiO₂ particles by colorimetry and SEM (Pinho et al., 2013; Smits et al., 2013). Nevertheless and to the best of our knowledge, this is the first study combining solid-state ¹³C NMR and analytical pyrolysis for assessing the effects of UVA irradiation and TiO₂ on the composition of diesel soot particles deposited on lime-based mortars. Moreover, there are no previous studies in the literature using real diesel soot deposits collected from combustion engines to test the photocatalytic action of TiO₂ on building materials under laboratory conditions.

Analytical pyrolysis is a powerful tool widely used for the direct characterisation of organic mixtures with diverse origin which, owing to their complexity, are difficult to analyse by both conventional destructive or non-destructive methods (González-Pérez et al., 2014). In fact it has become a valuable tool for the characterisation of complex carbonaceous matrices, including soot and urban dust on building surfaces (De la Rosa et al., 2008; Pereira de Oliveira et al., 2011). The solid-state ¹³C NMR has been widely used in the characterisation of refractory organic matter forms in soils and sediments and more recently has been successfully applied to study the composition of pyrogenic carbon, including soot and other forms of black carbon (De la Rosa et al., 2008; De la Rosa and Knicker, 2011).

2. Materials and methods

2.1. Sample preparation

In this work, lime-based mortars were prepared with different concentrations of TiO₂ and coated with diesel engine exhaust soot. These soot particles were collected from diesel automobile pipes in Lisbon city centre (Portugal) using a smooth brushing.

The binder used for preparing the mortar samples was a commercial 5-year packaged lime putty with a bulk density of 1.35 kg dm⁻³. As provided by the supplier (C.T.S., Getafe, Spain), its chemical composition is: CaO (88.0–90.0%), MgO (0.0–0.5%), SiO₂ + Al₂O₃ + Fe₂O₃ (0.1–0.3%), and CO₂ (2.5–3.5%). In addition, a 45 ± 5% of water was added to the mix. The mineralogical composition of this lime putty is portlandite [Ca(OH)₂] (86.0–88.0%) and calcite [CaCO₃] (7.0–9.0%). The aggregate used was a commercial siliceous sand (0.08/2.00 mm particles) with a bulk density of 2.60 kg dm⁻³ supplied by BIC *Materiales y Conservación* (Pontevedra, Spain), in accordance with the requirements of the Standard Specification for Concrete Aggregates ASTM-C33 (2013).

The photocatalytic additive added to the mortar samples was a commercial titanium dioxide product (P-25) from Degussa AG (Frankfurt, Germany), consisting of predominantly nanocrystalline anatase with a specific surface area of 50 m² g⁻¹, a bulk density of 0.13 kg dm⁻³ and a particle size of approximately 20 nm.

Three mortar formulations with different concentration of TiO₂ (0, 2.5 and 5 wt% with respect to the total solid content) were prepared (Table 1). For each formulation, three mortar samples of 6 cm × 6 cm × 2 cm were manufactured as described in Lucas et al. (2013) and

Table 1
Abundance (g kg⁻¹) of the lime putty, sand and TiO₂ used in the preparation of the lime-based mortars.

Sample ID	Lime putty (g kg ⁻¹)	Sand (g kg ⁻¹)	TiO ₂ (g kg ⁻¹)
L0	250	750	0
L2.5	244	731	25
L5	238	712	50

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