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Study of innovative photocatalytic cement based coatings: The effect of supporting materials

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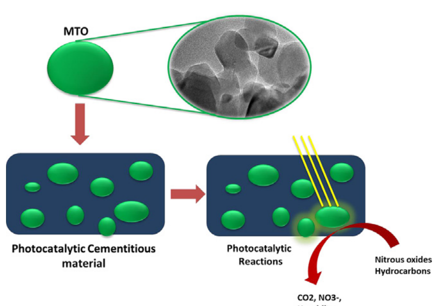
HIGHLIGHTS

- Photocatalytic cement coating with innovative UV and Visible active powder.
- NO oxidation experiments to test the influence of supporting materials.
- Over 99% and 50% reduction under UV and Visible irradiation respectively.

GRAPHICAL ABSTRACT



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ABSTRACT

For an ideal photocatalytic active building material, the substrate, on which the photocatalytic material is deposited, should neither interfere with nor affect its photocatalytic activity. In the present work, photocatalytic cement based coatings were immobilized on the surface of three different building substrates: gypsum, plywood and glass. The purpose was to investigate the effect of the substrates material on the photocatalytic activity of the corresponding end products against NO. In addition, the effect of the coatings composition and the selected illumination source (UV & Vis) on the material's photocatalytic behavior was also studied. Results displayed a slightly higher photocatalytic activity for the cementitious coatings on the glass substrate compared to the ones obtained on gypsum and plywood substrates, Overall, both cement based coatings, with 5% w/w and 10% w/w photocatalyst (Mn doped TiO_2), presented sufficient photocatalytic activity under either UV or Vis irradiation in the NO abatement. The latter (10% w/w) exhibited, as expected, a slightly better performance due to higher concentration, as monitored by the corresponding photocatalytic degradation rate parameters (n% and r) value.

1. Introduction

Titanium dioxide (TiO_2) heterogeneous photocatalysis is nowadays proved to be a very promising advanced oxidation process for the de-pollution and cleaning indoor and outdoor air, exhibiting unique advantages over conventional remediation technologies. A significant number of empirical studies nowadays display the unique photocatalytic properties of TiO_2 structures, with particles size of some nanometers, high surface area and high density of surface coordination, to oxidize nitrogen oxide (NO), to nitrogen dioxide (NO_2) and then to nitric oxide (HNO_3), as well as conversion of volatile organic compounds (VOCs) to CO_2 and H_2O under

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ultraviolet (UV) irradiation [1–9]. In most reported cases, the TiO_2 material was immobilized on different types of substrates including glass, beads, hollow tubes, fabric, silica gel, etc so as to avoid filtration stems [10].

Over the last decade, the incorporation of the TiO_2 photocatalyst into construction materials such as cement based products, or its immobilization onto the external surfaces of others, such as construction tiles, has become an appealing challenge for exploiting the unique properties of the photocatalytic oxidation (PCO) process and establishing its practical application into the removal of air pollutants in urban areas [11]. Usually, the following methods are applied to incorporate TiO_2 photocatalysts into cementitious materials: 1) mixing TiO_2 particles during cement making; 2) direct painting of a TiO_2 suspension solution onto cementitious matrix surface; 3) Sprinkling of TiO_2 photocatalyst onto fresh cementitious materials surface.

Nowadays a significant number of laboratory studies [9,12,13] as well as several pilot projects attest the depollution effectiveness of several photocatalytical active construction materials [6,14]. In addition, some real-site projects have been carried out lately, in which the photocatalytic air purification effect of cementitious materials has been reported under real complex environmental conditions [15,16].

Over the last years attention has been also paid to the role of several external and internal parameters on the aftermath photocatalytic behavior and performance of the materials under examination. The aim was to investigate the effectiveness that a practical application of such photocatalytically active construction materials might have on the air purification objective, along with the preparation and photocatalytic examination of the materials. A number of studies have shown that both the experimental set-up and the adopted photocatalytic measurement procedure can play a significant role on the photocatalytic behavior and performance of materials and therefore influence the pollutants degradation rate. In addition, it has been proved that several external parameters such as the pollutants nature, mixture, initial concentration, environment relative humidity, wavelength of the selected light of radiation and its intensity, as well as several internal ones like the amount of the semiconductor incorporated into the construction material, the particle size and method of application affect the efficiency of the photocatalytic process.

Nowadays, it is the interest of several research studies to investigate and attest the photocatalytic performance of such materials under real environmental conditions (since a number of related issues remain still unresolved). For example, as the majority of studies deal with high level of pollutant's initial concentration (thousands of ppbs), which are rarely found in outdoor and indoor real urban environments [2,5] elaborate studies on more realistic pollutant levels (some hundreds of ppbs) are scarce. Furthermore, the effect of the adopted humidity levels on the photocatalytic performance dependence on the material itself as well as on the adopted experimental conditions is debatable [5,17–20]. Martinez et al. 2011 [21,22] showed that the relationship between the increasing humidity levels and the systems performance was determined by the mortar and glass nature of the substrates and the initial concentration levels of the NO air pollutant. Similar inferences are drawn for the effect of the adopted light conditions. In this case, the question of the role of the transition metal ions doping into the TiO_2 matrix and its contribution to suppress the charge carrier recombination rate and facilitate the onset shift in the band gap absorption to the visible region has been raised. All these demand further inquiry on the development, test and improvement of such photocatalytically active systems under real-world experimental conditions. Along these lines we have published results on the role and efficiency of a visible light photocatalyst (TiO_2 doped with Mn) mixed with calcareous filler in different concentrations and deposited on 25 cm × 25 cm glass panels to degrade inorganic priority pollutants, e.g. NO, upon irradiation with a commonly used indoor light and have shown that the photocatalyst was able to degrade up to 95% of NO after 6 h of irradiation, without any significant photocatalyst inactivation [23].

However, on the preparation of photocatalytically active construction materials, among the parameters receiving increasing interest over the last years require attention is the substrates nature. This is one of the major concerns on many photocatalytic studies to utilize suitable sample holders that will remain inactive and will not inhibit or enhance the photoactivity performance/activity of the final material when powders, paints or thin films are deposited on their surface. In their work, Bianchi et al., 2012 [24], investigating the interactions between photoactive powder coatings and supporting materials, displayed the existence of a strong dependence between the materials and the nature of the supporting material. According to their results, glass and Teflon supports provoked an important decrease of the material photoactivity while steel supports were found to have a positive effect on the materials performance.

Attempting to cast further light onto the substrates-nature-quest, in the present paper we examine the ability/efficiency of laboratory made photocatalytic cement based coatings mixed with Mn-doped TiO_2 named MTO, deposited on three different substrates (glass, plywood and gypsum) to photocatalytically remove NO from an air environment. The photocatalytic performance of the materials was evaluated under ambient environmental temperature and humidity conditions specified in the follow section as well as under a low (~250 μg/m^3) initial pollutant concentration to provide an inside in this area of interest. In addition, the influence of two parameters, namely the amount of the MTO photocatalyst incorporated into the cement coating and the type of the light irradiation employed (UV and Visible), on the photocatalytic efficiency of the materials, were also investigated.

2. Materials and methods

2.1. Materials

Chemicals for the preparation of MTO nanoparticles were purchased from Aldrich and were of analytical reagent grade. Conventional commercially available cement coating and gypsum, plywood, glass which were used as substrates.

2.2. Methods

2.2.1. Preparation of MTO

MTO used for the preparation of photocatalytic cement coating, was synthesized and characterized in previous works along with the preparation details and the procedures applied for the synthesis of the TiO_2 powders doped with different concentrations of manganese [23].

2.2.2. Preparation of photocatalytic cement based coatings

In the present study, an optimum MTO powder (0.1% Mn-doped TiO_2) was added in cement coatings and applied on the surface of three different substrates (gypsum, plywood and glass panels of 0.25 m × 0.25 m). For the preparation of the applied photocatalytic cement coatings, a 5% and 10% w/w amount of the MTO photocatalyst was embedded in commercial cement coatings.

2.3. Characterization

Surface morphology and elemental analysis of the photocatalytic cement powders were carried out using Scanning Electron