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The effects of silica/titania nanocomposite on the mechanical and bactericidal properties of cement mortars

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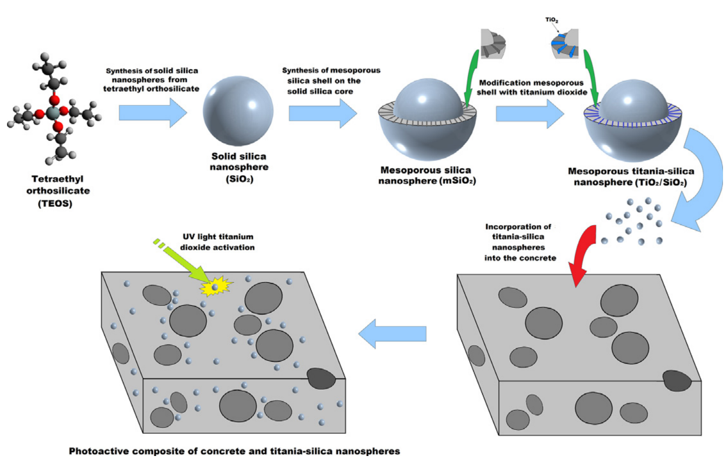
HIGHLIGHTS

- Silica/titania ($mSiO_2/TiO_2$) core-shell nanocomposite structures are used to improve properties of cement mortars.
- Inclusion of $mSiO_2/TiO_2$ improved the compressive strength and reduced water absorption of cement mortars.
- Application of $mSiO_2/TiO_2$ structures simultaneously, demonstrated the properties of nanosilica and titanium dioxide.
- Cement mortars incorporated with $mSiO_2/TiO_2$ exhibit relatively good bactericidal properties.

GRAPHICAL ABSTRACT



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ABSTRACT

The scope of the study is to test the influence of nanocomposite silica-titania ($mSiO_2/TiO_2$) core-shell structures on the mechanical and bactericidal properties of cement mortars. Nanocomposites are widely applied in many fields of science however, cement-based composites are mainly modified with single type of nanostructures. The goal of the presented work is to obtain a nanocomposite which exhibits the positive properties of both nanomaterials, while diminishing the negative impacts of each of the nanomaterials applied separately. The study shows that application of silica-titania ($mSiO_2/TiO_2$) core-shell nanostructures simultaneously demonstrated the properties of nanosilica and titanium dioxide and thus the nanomaterial behaved not only as a filler to improve the microstructure and activator to promote pozzolanic reaction, but also exhibited self-cleaning and bactericidal properties when exposed to UV light. The observed improvement of compressive strength was caused by the presence of nanosilica (acting as a core) while titanium dioxide (shell) exhibits photocatalytic activity.

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1. Introduction

In recent decades sustainable engineering and environmental issues have become a major concern, on a global scale. The increased emission of gasses in large urban centres has caused problems with pollution on a level previously unknown. The quality of people's lives, (especially in big agglomerations) has become seriously impaired by factors such as air pollution from vehicle exhausts and diseases caused by microorganisms [1]. There is therefore a growing concern, which has attracted the attention of governments, industry, and researchers, with methods for developing photocatalytic mortars capable of reducing pollutant concentrations in indoor air and contributing to more sustainable construction. Titanium dioxide (TiO_2), which has received considerable attention in the last few years, has revealed the ability to decontaminate pollutants via photocatalytic processes. The use of cementitious materials as a photocatalyst supporting media is very effective, due to its strong binding ability [2]. Furthermore, the porous structure of hardened cement paste allows the photocatalyst to react with the pollutants, thus facilitating photocatalytic conversion [3].

To date, a number of researchers have investigated and demonstrated the application of nanotitania in cement composites. The use of titania nanoparticles has been tested not only in Portland cement concretes [4], but also in autoclaved aerated concretes [5], pervious concretes used for parking lots [6] and self-compacting concretes (SCC) [7]. The influence of nanotitania on the inherent properties of hardened cement pastes and mortars has still not been fully examined and controversy still exists as to whether the addition of TiO_2 has a certain pozzolanic activity or whether it acts only as a fine non-reactive filler [8]. A study undertaken by Jalal et al. [9], in which TiO_2 was used as a partial replacement for cement at up to 4 wt%, showed an acceleration of C–S–H gel formation at the early age of hydration, as a result of increased crystalline $Ca(OH)_2$. Consequently, there resultant concrete had improvements in its microstructure and enhanced strength. A significant enhancement in the degree of hydration in the early hydration period has also been reported by Chen et al. [10]. These researchers reported that TiO_2 acted as a non-reactive fine filler and did not have certain pozzolanic activity. It acted as potential nucleation site for the accumulation of hydration products [8,10–12]. Another unresolved aspect, is that of the influence of nanotitania on the mechanical properties of cement-based composites. There is common agreement that fine nano-TiO_2 particles have a short setting time and significantly improve the compressive strength of mortars at early ages, but the influence on the long term mechanical properties of cured samples is still in dispute. In this regard, some studies are mutually exclusive and lead to completely different conclusions. Studies undertaken by Essawy et al. [8] and Nazari et al. [13], report a positive influence of TiO_2 on compressive strength. Conversely, data presented by other researchers, shows that nanotitania does in fact improve compressive strength, but just at the early stages of curing and that after 28 days the mechanical properties tend to decrease [12,14–16].

Recently, a new approach for creating nano-admixtures in cement-based composites – the synthesis of nanocomposites composed of different nanomaterials – has gathered noticeable attention. Based on the literature, it can be concluded that combining nanosilica (which has significant effects on the mechanical properties of cementitious composites [17–19]) and titanium dioxide (which exhibits self-cleaning properties [20]) can result in nanocomposites which can improve both of these properties when incorporated into cement-based composites. The photocatalytic properties of nanosilica-titania dioxide core shell structures have been reported by Cendrowski et al. [21] and Augustyniak et al. [22]. Moreover, silica/titania nanospheres have already been proposed as potential admixtures for cementitious composites, by Kamaruddin et al. [23], although so far there have been no studies devoted to their performance in a cementitious composite.

The scope of this study is to test the influence of nanocomposite silica-titania ($mSiO_2/TiO_2$) core-shell structures on the mechanical and bactericidal properties of cement mortars. The goal of the work presented was to obtain a nanocomposite which exhibits the positive properties of both nanomaterials, while diminishing the negative impact of each of the nanomaterials applied separately. It is presumed that the nanosilica (core) will act not only as a pore filler to provide nucleation sites and modify the microstructure of the cement matrix, but also as a contributing agent to promote a pozzolanic reaction, hence increasing the mechanical properties and refining the microstructure of the cement matrix. Furthermore, it is expected that the mesoporous shell containing titanium dioxide will exhibit photocatalytic and bactericidal properties.

2. Materials and methods

2.1. Materials

Rapid Hardening Portland Cement CEM I 42.5R, conforming to standard EN 197-1 was used, as purchased. The chemical composition of the cement is presented in Table 1. Fine quartz aggregate sand of 0/2 mm, consistent with EN 196-1, and tap water, conforming to EN 1008, were used. For comparison of the bactericidal properties of cement mortars, a commercially available titanium dioxide nanomaterial, Aeroxide® P25, with an average elementary crystallite of 21 nm and surface area of 50 ± 15 m^2/g, was used.

2.2. Synthesis of core-shell mesoporous silica nanospheres ($mSiO_2$) modified with titanium dioxide ($mSiO_2/TiO_2$)

Mesoporous silica core-shell nanosphere synthesis and functionalization with concentrated Titanium (IV) butoxide (TBT) has been previously described [21,24]. A schematic synthesis of nanomaterials is presented in Fig. 1. In order to create a core-shell, mesoporous nanospheres functionalized with titanium dioxide were prepared in a three step procedure. The first step was conducted according to a modified Stöber sol–gel: 2.5 mL of ammonium ($NH_3{\cdot}H_2O$) and 50.0 mL of ethanol (EtOH) were mixed together. The mixture was placed in a sealed reactor and stirred with a magnetic stirrer. After 30 min of mixing, 1.5 mL of tetraethyl orthosilicate (TEOS) was added. After TEOS addition, the suspension was stirred for 24 h. In order to separate solid silica nanospheres from the suspension, the mixture was evaporated.

In the second step, a mesoporous external layer on the as-produced silica spheres was synthesized. A mixture of 160 mg hexadecyl(trimethyl)azanium bromide (CTAB); 0.45 ml $NH_3{\cdot}H_2O$; 80 mL EtOH; 100 mL H_2O was prepared. 200 mg of silica nanospheres were dispersed in the prepared CTAB mixture . After obtaining a stable silica core dispersion of 0.28 mL, TEOS was added and the mixture was stirred for another 24 h. Next, the suspension was evaporated and the solid product was annealed in air at 600 °C for 3 h, in order to remove the surfactant from the mesopores [21,24].

The last step focused on the functionalization of mesoporous silica spheres with titanium dioxide. Functionalization was realized through the ultrasonic dispersion of 100 mg of silica nanospheres in 2 ml of concentrated Titanium(IV) butoxide (TBT). The suspension obtained was sonicated for 3 h in anhydrous conditions at 45 °C. Next, to purify the nanospheres from an excess of the titanium dioxide precursor, the suspension was diluted with n-propanol and centrifuged (8000 rpm for 10 min). Washing and centrifugation with n-propanol was repeated twice. After purification, nanostructures filled with TBT were treated with ethanol to hydrolyze the titanium dioxide precursor. Finally, the sample was evaporated and heated in air flow at 400 °C for 4 h, in order to transform the titanium dioxide into the anatase phase [21,24].

2.3. Photocatalytic decomposition of Rhodamine B

The photoactivity of $mSiO_2/TiO_2$ was examined via the photocatalytic decomposition of Rhodamine B. The photocatalytic reaction was carried out in an inner-irradiation-type reactor with an inner water cooling jacket. A mercury lamp of 150 W was used as the light source. The loading of the $mSiO_2/TiO_2$ was 50 mg/dm^3. For the reaction of the photocatalytic dye decomposition, 700 cm^3 of rhodamine B solution was used, with an initial concentration of 50 mg/dm^3. The mix-