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Novel 'Pickering' modified TiO_2 photocatalysts with high De-NOx efficiency

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ABSTRACT

Modified TiO_2 nanoparticles were prepared by a Pickering emulsions route with the use of hydrophobic (oleylamine) and hydrophilic (polyethylene glycol) organic surfactants and their combination, as well. The attachment of modifiers to the TiO_2 nanoparticles was proved via FT-IR and thermal analysis. Thicker modifier layer was formed on the TiO_2 surface but lower average particle size was attained when amphiphilic modification was applied that was revealed by TEM analysis and dynamic light scattering, correspondingly. The amphiphilic modification permitted control of the hydrophobic properties of the TiO_2 nanoparticles so that their incorporation in cement matrix led to preparation photocatalytic cement materials with superior De-NOx efficiency.

1. Introduction

The last years, Janus nanoparticles attracted increased attention of the scientific community since they possess outstanding properties which originate from their asymmetric structure or functionalization [1,2]. Two different types of physics or chemistry that occur on two different parts of the same particle inflame wide range of interesting applications like superstructures [3], tissue engineering, emulsions stabilization, catalysis, photonic crystals [4–6].

A variety of methods has been investigated concerning the synthesis of Janus nanoparticles such as phase separation, masking and self-assembly [7,8]. The real challenge yet is in development simple routes for preparation of large amounts of Janus nanoparticles. One of the very promising methods is nanoparticles confinement at the interface of two non-miscible solvents [1]. An indicative paradigm is Pickering emulsions which are stabilized through solid nanoparticles and not via surfactants [9,10]. More specifically, the solid nanoparticles accumulate at the interface of non-miscible liquids as a monolayer and inhibit in that way the coalescence of droplets [11].

Silica nanoparticles are widely utilized as emulsions stabilizers. Titania nanoparticles are also extensively used since they perform unique properties such as the increased energy gap, activation in environmental conditions, low toxicity and strength towards corrosion [5,11–15]. These unique properties have already promoted a wide range of studies concerning TiO_2 surface modification. Functionalized nanoparticles have been successfully applied for enhancement of photocatalytic activity in solar purification of water [16], oxidation of NOx air pollutants [17], reduction of CO_2 air pollutant [18], degradation of methylene blue [19] and atrazine [20]. As for the use of anisotropic nanoparticles use in photocatalysis field, it was shown [7] that development of asymmetric Au-TiO_2 nanoparticle photocatalysts contributes to enhanced hydrogen production because of strong plasmon fields created on noble metal interface. Furthermore, according to [21,22], the anisotropic Au-TiO_2 nanoparticles provide increased photocatalytic activity due to acceleration of charge separation.

Pickering emulsions stabilization depends on various parameters such as particles size, concentration, hydrophilicity/hydrophobicity, shape, wetting ability, pH, intermolecular interactions, ionic strength and coagulation, etc. [23–27]. As for the superhydrophilic/superhydrophobic properties, they resulted in increased agglomeration, while the semi-hydrophobicity or amphiphilicity (combined hydrophobic and hydrophilic properties) could lead to raised emulsions stabilization efficiency.

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This hypothesis was assumed in [1] since it was proven that TiO_2 modification with hydrophobic and hydrophilic phosphonic compounds contributed to enhanced emulsions stabilization.

This study is focused on the effect of hydrophilic, hydrophobic and combined hydrophilic and hydrophobic modification of TiO_2 nanoparticles on the photocatalytic activity of composite cement products regarding the oxidation of NO pollutant. The surfactants used were the hydrophobic oleylamine (OM) and the hydrophilic polyethylene glycol (PEG). The synthesis procedure of modified nanoparticles was conducted via Pickering emulsions which were developed through a biphasic solvent system of toluene and water.

We suppose that amphiphilic modification will result in tunable hydrophobic properties which will not impede modified nanoparticles incorporation in hydrophilic matrix of cement. Moreover, the amphiphilically modified titania will be promoted with a controllable way to the surface of cement thus enhancing air pollutants access to photocatalysts and oxidation, as well.

2. Materials and methods

2.1. Materials and preparation of the samples

Commercial TiO_2 powder P25 (Evonic-Degussa) was used as a photocatalyst. The organic solvent toluene (purity 99.5%) was purchased from Merck, Germany. The oleylamine and polyethylene glycol with molecular mass 2000, were obtained from Sigma-Aldrich and Panreac respectively. Bi-phase system of toluene/water solvents was used in all cases for TiO_2 modification.

2.1.1. Preparation of OM-capped TiO_2 nanoparticles

Initially, a homogeneous aqueous suspension containing 1 g of commercial P25 photocatalyst and 100 mL of deionized H_2O was prepared. To achieve better suspension homogeneity, tip sonicator (Hielseher, UIP 100hd) was used at 50% amplitude for 3 min. Also, a specific amount of oleylamine (Table 1) was mixed with 100 mL of toluene and stirred at 500 rpm for 20 min. Then, the organic solution was transferred dropwisely into the aqueous TiO_2 dispersion and the final emulsion was kept under vigorous stirring (~2000 rpm) at 40 °C for 16–18 h. After the termination of stirring, the samples were left to cool at room temperature until the two phases of water\toluene were clearly distinguished. It was observed that modified nanoparticles were initially accumulated in the toluene but after a few minutes they were gathered at the water/toluene interface. The modified nanoparticles were collected through centrifugation (8000 rpm, 3 min) and twice washed with acetone. Finally, they were dried at room temperature for 24 h. The sample was named OM1.

2.1.2. Preparation of PEG-caped TiO_2 nanoparticles

In this case, specific amount of polyethylene glycol (Table 1) and 1 g of commercial P25 photocatalyst was mixed with 100 mL of deionized water in tip sonicator (Hielseher, UIP 100hd) at 50% amplitude for 3 min. Then, 100 mL of toluene was added dropwise to the mixture and the final emulsion was kept under vigorous stirring (2000 rpm) at 40 °C for 16–18 h. After that, it was left to cool at room temperature. No water/toluene phase separation was observed. The modified nanoparticles were collected through centrifugation (8000 rpm, 10 min) and twice washed with acetone. Then, they were left to dry at room temperature for 24 h. The sample was named PEG1.

2.1.3. Preparation of OMPEG-caped TiO_2 nanoparticles

A mixture was prepared containing 1 g of commercial P25 photocatalyst, a specific amount of hydrophilic compound polyethylene glycol (Table 1) and 100 mL of deionized H_2O using tip sonicator (Hielseher, UIP 100hd) at 50% amplitude for 3 min. Also, a specific amount of oleylamine (Table 1) was mixed with 100 mL of toluene at 500 rpm for about 20 min. Then, the solution was transferred dropwise to the mixture with the photocatalyst and the resulting emulsion was kept under vigorous stirring (~2000 rpm) at 40 °C for at least 18 h. After that, it was left to cool at room temperature. With time, the modified nanoparticles were observed to equilibrate at the interface of water/toluene. They were collected through centrifugation (8000 rpm, 3 min), twice washed with acetone and dried at room temperature for 24 h. The sample was named OMPEG1.

2.2. Preparation of photocatalytic cement samples

White cement was kindly provided by TITAN CEMENT COMPANY S.A. The preparation process of photoactive cement tiles was described in detail in [27]. Shortly, pure or modified P25 nanoparticles and white cement were initially dry mixed. The mixtures contained 2.5 wt% of titania. Then, water was added in weight ratio water/dry mix = 1/1. After mixing, the pastes were transferred to specially prepared moulds and let to harden for 3 days at room temperature. The nomination of the titania loaded cement samples investigated in the present work is presented in Table 1.

2.3. Methods of characterization

Fourier Transform Infrared Spectroscopy (FTIR) was used to investigate the bond formation between surfactants and titania nanoparticles with the help of EQUINOX 55/S, BRUKER operating in diffuse reflectance mode. The samples consisted of 95% KBr and 5% photocatalyst were placed in a sampling cup and were scanned in wavenumber range 400–4000 cm^{-1}. The thermal behavior of modified nanoparticles was determined by Thermal Gravimetric Analysis using Perkin-Elmer Pyris TGA/DTG instrument. Dynamic Light Scattering technique was employed to determine the particle hydrodynamic diameter of modified nanoparticles in chloroform and water solvents through Zeta-sizer Nanoseries, Malvern instrument. The BET specific surface area of the initial and modified TiO_2 nanoparticles was measured using Quantachrome Autosorb-iQ instrument. The XPS spectra of the samples were obtained with ultrahigh vacuum VG EXCALAB 210 electron spectrometer using MgKa (1253.6 eV) as radiation source. Morphological characterization of composite materials was conducted using Transmission Electron Microscopy (TEM, Philips CM20) operated at 200 kV and equipped with the image filter GATAN GIF 200. The Finally, the photocatalytic activity of the prepared titania and titania loaded cement samples was examined through NO oxidation based on ISO DIS 22197/1:2007 standard method. The experimental set up used for measurement of the NO, NO_2 and NOx = NO + NO_2 concentrations is schematically presented in [27]. The De-NOx ability was evaluated by the decrease of the NOx concentration from its initial value (1 ppm) in the gas media. The photocatalytic activity was determined under UV-A (main peak at 350 nm) with intensity 10 W/m^2. The photonic efficiency ζ (mol/einstein) of the photocatalytic materials under UV irradiation was evaluated through the ratio of the number of oxidized gas molecules to the number of incident photons for the entire illumination period according to the Eq. (1):

$$\zeta = \frac{\int_{t_0}^{t_1} AX * 10^{-6} dt}{q_{n,p} T} \quad (1)$$

Where A (mol/s) is the constant related to the gas flow rate, X (ppm) is the instantaneous values either of NO (NOx) removal or NO_2 formation, $q_{n,p}$ (einstein/s) is the photon flux on the sample's surface, T (s) is the duration of the illumination period (Table 2).

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