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TiO_2 cement-based materials: Understanding optical properties and electronic band structure of complex matrices

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ABSTRACT

Different mortar mixes using TiO_2 P25 as photocatalyst have been prepared. The samples were characterized by UV–vis spectroscopy, X-ray photoelectron spectroscopy and Photoluminiscence spectroscopy. Also, determination of hydroxyl radicals and degradation tests of NOx under visible and UV light have been performed. The results obtained have allowed determining the band edges, Urbach energies and valence band tail sizes, directly related to the energy levels present in the TiO_2-cement based materials. Therefore, the schema of the electronic structures of the reference TiO_2-photocatalyst and the three TiO_2-cement based samples have been constructed. The photocatalytic efficiency has been evaluated according to these energy levels, being able to conclude that in some cases, as the mortar with slags, the chemical composition seems to prevail over the effect of the optical parameter and electronic band structure.

1. Introduction

Combining TiO_2 nanoparticles with cementitious binders is undoubtedly one of the most promising topics in the field of environmentally friendly building materials with multifunctional attributes. Indeed, the incorporation of photocatalyst provides air decontamination, self-cleaning, self-sterilizing, and anti-fogging properties to construction materials [1–8]. Currently, the most common applications of photocatalytic TiO_2 in combination with cementitious matrices include coatings in the form of films and powders into cementitious supporting material. Moreover, the effect of cementitious substrate has even characteristics that can facilitating the photocatalytic process, as the porous structure of the hardened cement binders and strong binding property and compatibility of their alkaline pH with TiO_2.

One of the most important topics for an adequate application of TiO_2 photocatalytic materials is the analysis of its optical characteristics. The optical parameters of photocatalytic materials are of considerable interest because their efficiency depends of light absorption and consequent conversion to an excited state of surface. The initiation of a photocatalytic reaction requires a minimum photon energy that exceeds the band gap of the material in order to trigger the inter-band transition of electrons between the highest occupied molecule orbital and the lowest unoccupied molecule orbital. For this reason, the characterization of optical parameters is essential for improving the efficiency of photocatalytic materials.

UV–vis spectroscopy has been extensively used to characterize optical absorption properties on photocatalytic materials [9–11]. The optical excitation of the electrons from the valence band to the conduction band is evidenced by an increase in the absorbance at a given wavelength (band gap energy). The linear section in the diffuse reflectance spectra is taken for measuring the band gap energy, which is one of the most important results in optical characterization of photocatalytic materials. Besides, X-ray photoelectron spectroscopy get further insights into the possible modifications of electronic structures of photocatalytic samples related with the formation of localized states that trap the photoexcited charge carrier and can narrow the band gap of TiO_2-photocatalyst. Photoluminescence spectroscopy is also essential to identify energy defect states in a material and provide information about the efficiency of charge carrier trapping, immigration and transfer [12,13]. The combination of all techniques allows defining the complete electronic structure, optical and photochemical properties of photocatalytic materials, which allow understand the overall photocatalytic process [11,13–15].

It is generally acknowledged that the photocatalytic performance of TiO_2 samples can be greatly influenced by the chemical

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composition of the cementitious supporting material [7,10,16]. However, a direct correlation of the chemical properties with the optical properties and its influence on overall photocatalytic performance is rather difficult and contradictory results can be found.

In this work, the inherent relationships between the optical parameters, electronic band structure and photocatalytic activity of TiO_2 cement based materials are discussed in detail. Also this work can help us to further understand the transfer and separation behaviour of photo-induced charge carriers which are favourable to investigate and prepare functional semiconductor materials with high photocatalytic activity.

2. Experimental

2.1. Materials

ASTM Ordinary Portland cement Type I 52.5 R and cement Type III/C, including 81–91% of slag were used in this study. Two type of sand, siliceous and calcareous were used to cast the mortars. As photocatalyst, TiO_2 P25 (75% anatase and 25% rutile, Degussa, Germany) was added to the cement mixes.

2.2. Preparation of the mortar samples

Four different normalized mortar mixes (water/cement ratio = 0.5/1 and cement/sand ratio = 1/3) have been cast with the previous materials. The mixing procedure was carried out following the standard UNE-EN-196-1. For sample production, 2% TiO_2-photocatalyst in weight of cement were mixed as dry powders with the corresponding cement. Reference cement mortar samples without photocatalyst were also made.

Mortars were cast in Petri dishes moulds with 90 mm diameter rand 10 mm height, and were cured in humid chamber during 28 days. The composition of prepared mortars is shown in Table 1.

2.3. Characterization of materials

UV-vis absorption spectra of reference cement based samples without TiO_2 (CM), TiO_2-cement based materials (TiO_2-CM), and the corresponding pure TiO_2 photocatalyst were obtained using a Shimadzu UV-2600 UV/VIS/NIR spectrometer equipped with a diffuse reflectance accessory sphere. The photoluminescence spectra were recorded using a PerkinElmer LS55 fluorescence spectrometer. The valence band spectra of samples were analyzed using X-ray photoelectron spectroscopy (Thermo Escalab 250, a monochromatic Al Ka X-ray source). All binding energies were referenced to the C 1s peak (284.6 eV) arising from adventitious carbon.

The photocatalytic activity of TiO_2-CM samples was investigated by monitoring the degradation of nitrogen oxide (NOx) under visible and UV radiation. NOx removal activity was tested based on the requirements of ISO standard 22197-1. NO gas was diluted in pure air until reaching an initial concentration of 1000 ± 50 ppb including a small amount of NO2 (<7%). Two mass flow controllers were used to prepare the mixture supplying a flow rate of 3 L/min. The tests were performed at 22 ± 2 °C and a relative humidity of 40 ± 2%. The sample was illuminated for 30 min. The NOx concentration of the gas was measured using a chemiluminescence analyzer (AC–32 M, Environment S.A.). The calculation of the amount of NOx removal during the irradiation by the sample was calculated using below equations.

$$NOx_{removal}\left(\mu mol/min \cdot cm^2\right) = \left(f/22.4\right) \cdot \left[\int (NO)\,dt - \int (NO_2)\,dt\right] / (A \times T) \quad (1)$$

$$NO_{removed} = \int ([NO]_0 - [NO])dt \quad (2)$$

$$NO_{2formed} = \int ([NO_2] - [NO_2]_0)dt \quad (3)$$

Where $[NO]_0$ inlet concentration of nitrogen monoxide (ppm), [NO] outlet concentration of nitrogen monoxide (ppm), $[NO_2]_0$ inlet concentration of nitrogen dioxide (ppm), $[NO_2]$ outlet concentration of nitrogen dioxide (ppm), t time of removal operation (min), f flow rate converted into that at the standard state (0 °C, 1.013 kPa) (L/min), A surface area of cement paste samples (cm^2), and T duration of irradiation for test.

The measurement of photo-induced $OH^\bullet$ formed on the photo-illuminated samples was carried out using terephthalic acid (TA) fluorescence probe method. This fluorescence probe readily reacted with the $OH^\bullet$ formed to produce the highly fluorescent product, 2-hydroxyterephthalic acid (TAOH) [17]. A previous study [18] has demonstrated the viability of using this method to quantify the complete $OH^\bullet$ production from the photogenerated holes at the photocatalytic mortar surfaces. To determine the $OH^\bullet$ production of TiO_2-CM samples, 25 mL of TA (2 mM) in diluted NaOH aqueous solution (0.02 M) were added into the test cells onto the specimens, and were irradiated for 20 min under continuous stirring. FL intensity of the solution was measured at 425 nm at different times of irradiation using the excitation with the wavelength of 315 nm. Fluorescence spectra of solutions were measured with a fluorescence spectrophotometer (Perkin-Elmer, LS-55). The detailed procedure of this experimental test is described in Ref. [18].

The photocatalytic assays were performed using as a UV light lamp (Philips actinic BL TLD −14 W) and visible light lamp (Philips master TLD 15 W/840). The light intensity was adjusted to 10 ± 0.2 W/m^2.

3. Results and discussion

The UV–vis reflectance spectra of the samples analyzed are shown in Fig. 1(a). The absorption spectra of the samples are obtained from reflectance data using the Kubelka–Munk equation, $F(R) = (1 - R)^2/2R$ [19] (Fig. 1(b)). From these figures, it can be observed that the optical spectra of TiO_2-cement based samples (TiO_2-CM) can be divided into three main regions; there are a weak absorption region (250–325 nm), an absorption edge region (325–350 nm), and a region of strong absorption (350–800 nm). The strong absorption of pure TiO_2-photocatalyst and TiO_2-CM between 250 and 350 nm (3.5–5 Ev) is consistent with the characteristic band–band transition of TiO_2. The absorption edges of TiO_2-CM samples and pure TiO_2 photocatalyst coincide at the same starting point (~325 nm), which indicated that the measured absorption edge on TiO_2-CM samples may be attributed with the band gap transition of TiO_2. In contrast, reference cement samples without TiO_2 (CM) shown a quite stable absorbance for the all wavelengths, and only present a slight absorption edge at high frequencies (270–300 nm). Due to the wavelength absorption edge of CM samples does not correspond with the pure TiO_2 photocatalyst, this absorption edge can only attributed to the colour of the samples.

In order to obtain the band edge (Eg) values of TiO_2-CM samples and compare with TiO_2 −photocatalyst, the Kubelka–Munk optical absorption coefficients [F(R)] were plotted using Tauc's relation (Eq. (4))

$$F(R)\,h\nu = (h\nu - Eg)^n \quad (4)$$

The product hν represents the energy of the incident photon and the exponent n depends on the type of transition, with an assigned