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Visible light TiO₂ photocatalysts assessment for air decontamination

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ABSTRACT

Different visible light responses of commercial TiO₂ photocatalysts are assessed for their application in air decontamination. To do that the modified TiO₂ catalysts were immobilized on borosilicate glass plates according to a dip coating method. Then, the photocatalytic performance of these plates was evaluated in a continuous gas flat plate photoreactor irradiated with visible light lamps using two representative air pollutants: nitrogen oxide and acetaldehyde. Working under visible light, the modified TiO₂ catalysts were compared by means of efficiency parameters: the true quantum efficiency, which relates the moles of degraded pollutant with the moles of the absorbed photons, and the apparent photonic efficiency, which relates the moles of degraded pollutant with the moles of incident photons. Also, the photocatalytic pollutants degradation by immobilized modified TiO₂ could be related with their optical properties, finding a clear correlation between them. These results are useful to decide which TiO₂ will be more efficient for a full scale air decontamination process under visible light illumination.

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1. Introduction

Heterogeneous photocatalysis represents an emerging environmental control option for the efficient removal of chemical pollutants that can be applied for water and air purification (Hoffmann et al., 1995). One of the limitations of this technology is that normal TiO₂ can only be activated by UV radiation (280–400 nm) that represents 4% of the total energy of the sun; meanwhile the visible light constitutes 45% of the solar radiation. On the other hand, the UV radiation amounts to only 0.001–0.05 W/m² in indoor lighting (Kuo et al., 2007). To extend the use of photocatalysis to visible light region, it is necessary to prolong TiO₂ radiation absorption to wavelengths corresponding to visible spectrum (400–700 nm). So far, several

modification methods of photocatalyst to amplify its absorption spectrum to visible radiation have been investigated and therefore, the applicability of heterogeneous photocatalysis has been extended (Banerjee et al., 2014; Chatterjee and Dasgupta, 2005; Dagher et al., 2013; Kisch and Macyk, 2002). Several commercial types of modified TiO₂ can be already found in the market for indoor visible light applications.

There are various types of modified TiO₂ active under visible light and different methods to perform the modification process. A first method is the treatment of TiO₂ with reductive hydrogen plasma (Van Durme et al., 2007). TiO₂ can also be sensitized by adsorbed dyes and semiconductors having lower band-gaps and more cathodic conduction bands (Demeestere et al., 2005). A third method is the TiO₂ doping with

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transition metals such as Fe, Cu, Co, Ni, Cr, V, Mn, Mo, Nb, W, Ru, Pt and Au (He et al., 2010). Finally, an alternative approach is the doping with non-metal anions, like nitrogen (Jo and Shin, 2010), carbon (Kuo et al., 2007) or sulphur (Nishijima et al., 2007).

In many studies employing modified TiO₂ with visible light absorption, the photocatalytic degradation of several volatile organic compounds (VOCs) and inorganic gases has been studied: nitrogen oxides (Yu and Brouwers, 2009; Lin et al., 2006; Nakamura et al., 2000), 2-propanol (Ihara et al., 2001), toluene (Fuerte et al., 2001; Ihara et al., 2001; Kubacka et al., 2009; Van Durme et al., 2007), acetaldehyde (Asahi et al., 2001; Iketani et al., 2004; Nishijima et al., 2007; Sakthivel and Kisch, 2003a, 2003b), acetone (Ihara et al., 2003), benzene (Sakthivel and Kisch, 2003a,b), carbon monoxide (Sakthivel and Kisch, 2003a,b), trichloroethylene (Demeestere et al., 2005; Jo and Yang, 2010), dimethyl sulfide (Demeestere et al., 2005) and dimethyl disulphide (Jo and Shin, 2010), methyl-tertiary butyl ether (Jo and Yang, 2010), acetic acid (Nishijima et al., 2007), and formic acid (Nishijima et al., 2007).

In the present work, different visible light absorption TiO₂ commercially available catalysts, one doped with carbon, another doped with nitrogen and two photocatalytic solutions ready to use, are studied. The carbon doping introduces new states close to the valence band edge of TiO₂ narrowing the photocatalyst band gap. In addition, carbonaceous species at the surface of the photocatalyst facilitates the absorption in the visible wavelengths as well as the high surface area of the doped TiO₂ promotes the adsorption of pollutants. Nitrogen doped titania could have either substitutional or interstitial N atoms in the TiO₂ matrix, resulting in a visible light response due to the electron transition from the localized N orbital to the conduction band or to the surface adsorbed O₂. One of the employed solutions is made of silver modified TiO₂. The noble metal doping increases the separation of photogenerated charge carriers and reduces the recombination rate of photoinduced electron-hole pair.

Two representative air pollutants are employed to assess the photocatalytic performance under visible light of the modified TiO₂ mentioned above: (i) NO as an inorganic contaminant and (ii) acetaldehyde as a simple structured organic pollutant. The nitrogen oxides (NO_x) are the generic term for a group of highly reactive gases, most of them emitted to air in the form of nitric oxide (NO) and nitrogen dioxide (NO₂). They are mainly formed in combustion processes and cause a wide variety of health and environmental impacts. The NO_x compounds are responsible for tropospheric ozone and urban smog through photochemical reactions with hydrocarbons.

Furthermore, NO_x together with SO_x (sulfur dioxide and sulfur trioxide) is the major contributor to the “acid rain”. On the other hand, acetaldehyde is one of toxic, irritant, and probable carcinogen VOC contaminant in indoor and outdoor environments. It is also a result of: (i) combustion processes, such as vehicle exhaust, tobacco smoke, and wood burning, and (ii) sources in homes including building materials, like laminate, linoleum, wooden varnished, and cork/pine flooring, plastic water based and matt emulsions paints, wooden, particleboard, plywood and chipboard furniture (Missia et al., 2010).

The photocatalysts were immobilized on borosilicate glass plates according to a dip coating method. The optical properties of the immobilized samples were determined in order to correlate the visible light absorption with the de-polluting capability. The performance of these systems was evaluated calculating the photonic and the quantum efficiencies, that correlate the contaminant reaction rate with the incident radiation flux and the absorbed radiation by the catalysts, respectively. The main objective of this work is to determine which photocatalyst will present the best pollution abating ability in a full scale application under visible light conditions.

2. Experimental

2.1. Sample preparation

Four types of visible light photocatalysts were acquired from the market: a powder doped with carbon, a powder doped with nitrogen and two liquid solutions ready to use for coatings. The measured BET area for the Carbon and Nitrogen doped TiO₂ powders were 251 m² g⁻¹ and 34 m² g⁻¹ respectively.

The immobilization of the TiO₂ powders and liquid suspensions was carried out according to a dip coating procedure on borosilicate glass plates. The TiO₂ powders load in deionized water to prepare the coating was 75 g L⁻¹. For every dip coating cycle, the glass piece was dried at 110 °C for 24 h and calcined at 500 °C for 2 h, repeating this procedure four times. Additionally, in order to increase the adhesion between the TiO₂ particles and glass, especially for employing the carbon doped catalyst, some plates were sandblasted. On the other hand, as the TiO₂ suspensions at natural pH precipitate quite fast, different suspensions at different pHs adjusted with nitric acid and sodium hydroxide were prepared, finding that the suspension at pH 1 for both TiO₂ powders were the most stable. Table 1 summarizes all prepared sample and the corresponding deposited photocatalyst mass per unit area. The given samples names are TiO₂-*m*-nL or TiO₂-*m*-nL-S, where *m* refers

Table 1 – Prepared samples and main characteristics.

Sample name	Type of catalyst	Number of layers	Glass surface	Suspension pH	Specific load (g cm ⁻²) × 10 ⁴
TiO ₂ -C-1 L	Carbon doped TiO ₂ powder	1	Smooth	6	3.75
TiO ₂ -C-4 L		4	Smooth	6	8.02
TiO ₂ -C-1 L-S		1	Sandblasted	1	1.06
TiO ₂ -C-4 L-S		4	Sandblasted	1	2.34
TiO ₂ -N-1 L	Nitrogen doped TiO ₂ powder	1	Smooth	6	2.12
TiO ₂ -N-4 L		4	Smooth	6	4.43
TiO ₂ -N-1 L-S		1	Sandblasted	1	0.965
TiO ₂ -N-4 L-S		4	Sandblasted	1	1.53
TiO ₂ -Ag-Sol-4 L	Silver modified TiO ₂ solution	4	Smooth	–	0.280
TiO ₂ -Sol-4 L	Visible light response modified TiO ₂ solution	4	Smooth	–	0.501

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