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Synthesis and photocatalytic activity of Mn-doped TiO_2 nanostructured powders under UV and visible light

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ABSTRACT

A straight forward, simple and inexpensive process has been developed by sol–gel method for the synthesis of manganese (Mn) doped and undoped TiO_2 photocatalysts. X-ray powder diffractometry (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) revealed the presence of structural nanoparticles with an average nanocrystalline size of about 20 nm. FT-IR/vis adsorption has shown enhanced sub-band-gap absorption as a function of Mn concentration. The photocatalytic activity of these materials was evaluated by the degradation of a basic Methylene Blue (MB) as organic contaminant. Mn-doped TiO_2 powder with molar ratio 0.1:100 was mixed with calcareous filler (5% and 10% respectively) and the photocatalytic activity was evaluated by the degradation of inorganic pollutants such as NO_x under UV and visible light.

1. Introduction

Titanium dioxide (TiO_2) has been widely studied particularly since the discovery of its photocatalytic properties by Fujishima and Honda in 1972 [1]. Some of the current promising applications for TiO_2 nanomaterials include its content in paints [2], and toothpastes [3], while it is used also for UV protection, in photocatalysis [4,5], in photovoltaics, in gas sensing, in electrochromics as well as photochromics [6]. As a catalyst, TiO_2 nanomaterials are very stable, nontoxic, cheap and have high photocatalytic reactivity in the elimination of pollutants in air and water [7]. A very important application of TiO_2 photocatalysts is in the purification of indoor and outdoor air [8]. Malodorous substances such as ammonia, hydrogen sulfide, formaldehyde, acetaldehyde, toluene, etc., constitute potential risks to human health and comfort. Fortunately, these dangerous volatile organic compounds (VOCs) oxidize in the presence of TiO_2 nanomaterials into harmless compounds such as CO_2 and H_2O under irradiation with UV and visible light [9–22]. The catalytic mechanism is based on the excitation of electrons from the valence band (VB) to the conduction band (CB) of the TiO_2, leaving holes in the Valence Band. These electrons (e^-) and holes (h^+) can then initiate redox reactions with molecular species adsorbed on the surface of the catalyst.

Titanium dioxide can have three different crystalline phases – *rutile* (R), *anatase* (A) and *brookite* (B). There are a large number of publications reporting on the effect of phase composition and particle size on the efficiency and the photocatalytic degradation of organic pollutants. Some demonstrate that *anatase* has a higher photocatalytic activity than rutile, while in others the best performance is related to rutile [23–27]. Many experimental data indicate that mixed phases, with small amount of rutile, can facilitate the separation of photogenerated charge carriers and this enhances the photocatalytic activity [28].

Anatase TiO_2 has an energy band gap of 3.2 eV and can be activated by UV radiation with a wavelength up to 387 nm thus limiting its application as a photocatalyst under visible light illumination. However, doped with transition metal ions, the TiO_2 matrix has been frequently reported to suppressing charge carrier recombination and facilitates the onset shift in the band gap absorption to the visible region, thus enhancing its photocatalytic activity [29]. Choi et al. performed a systematic study of TiO_2 nanoparticles doped with 21 metal ions by the sol–gel method and found that the presence of metal ion dopants significantly influenced the photoreactivity, charge carrier recombination rates, and interfacial electron-transfer rates [30]. Paola et al. have investigated the doping of Co, Cr, Cu, Fe, Mo, V and W into TiO_2 matrix prepared by wet impregnation method [31]. Nagaveni et al. reported an inhibitory

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effect for the dopants W, V, Ce, Zr, Fe and Cu prepared by the solution combustion method [32] while few researchers have claimed the enhanced activity for these dopants compared to undoped TiO_2 in photocatalysis [33]. Kumar and co-workers have studied the photocatalytic activity of aniline blue under UV/solar light for the dopants Mn^{2+}, Ni^{2+}, and Zn^{2+} into the TiO_2 matrix [34].

In this work, we report on the synthesis and characterization of TiO_2 nanomaterials doped with manganese (Mn) in different concentrations capable to absorb and activate under visible light irradiation. The Mn-doped TiO_2 (Mn:TiO_2) powders were prepared by a modified sol–gel method. The photocatalyst was synthesized [patent GR20090100724] following a few simple synthetic steps listed below with two different precursors namely titanium (IV) tetra-isopropoxide ($Ti\{OCH(CH_3)_2\}_4$) and titanium (IV) oxysulfate ($TiOSO_4xH_2O$). Photocatalytic material may be obtained with the same physical properties, the same structure and almost the same photocatalytic activity regardless of the above precursors involved. However, the titanium (IV) tetra-isopropoxide is expensive and the synthesis requires organic solvents which increase the price of the final product; also the synthesis is harder to scale up, in contrast with the titanium (IV) oxysulfate ($TiOSO_4xH_2O$) precursor applied here. To improve the photocatalytic activities we doped TiO_2 with manganese and carried out a study of its photocatalytic activity using UV and visible light as source of radiation with Methylene Blue (MB) as the test contaminant. These photocatalytic materials may be incorporated either into concrete surfaces or applied as coatings (i.e. in walls roofs and floors) for indoor depollution applications. They may also be applied in out-door applications (i.e. sidewalks, landscaping of buildings, parking lots, etc.), contributing to improved air quality and urban environments through the reduction of pollutant agents.

In the present work, we studied the photocatalytic activity of Mn:TiO_2 powders through the degradation of a basic MB organic contaminant. Further on we mixed the above photocatalytic powders with calcareous filler base coatings. Mn:TiO_2 powders alone as well as special coatings/overlays of calcareous base with 5% and 10% powder were prepared and studies were carried out on their photocatalytic activity using UV and visible light as source of radiation towards NO_x, as inorganic pollutant.

2. Experimental

2.1. Preparation of undoped and Mn doped TiO_2

Titanium (IV) oxysulfate hydrate ($TiOSO_4{\cdot}xH_2O$), manganese (II) acetate tetrahydrate, ≥99% and titanium (IV) tetraisopropoxide [$Ti(OCH(CH_3)_2)_4$] purchased from Aldrich were applied. The Mn doped TiO_2 was prepared by a modified sol–gel method. The photocatalyst was obtained by precipitating titanium dioxide on a sol of manganese dioxide, as shown in the flowchart of the synthesis employing $TiOSO_4$ of Fig. 1. The hydrated manganese dioxide sol was obtained by mixing the required volumes of manganese acetate, i.e. $Mn(CH_3COO)_2$, 0.1 M and potassium permanganate $KMnO_4$, 0.1 M solutions and stirring the mixture for 24 h at room temperature. The obtained sol was mixed with a solution of $TiOSO_4$. The concentration of $TiOSO_4$ in the final solution was 0.1 M. The colloidal solution was stirred (Fig. 1/step1) at room temperature for 48 h, in order to obtain the adsorption equilibrium. During this phase an exchange of Mn with Ti occurs and the final sol was a mixture of both dioxides. After this step, the remaining Ti^{4+} ions were forced to precipitate by adding NH_3 solution so that the final pH was 7 (step 2). Gel so formed was stirred continuously at room temperature for aging (48 h). After aging the sol was separated using centrifuging or alternatively it was filtered under vacuum, to obtain a powder (steps 3–4). The powder was than washed (step 5) with distilled water until free of sulfate and ammonium ions. The powder was free of sulfate and ammonium ions when the test of sulfate and ammonium was negative. If the test was positive, the procedure (step 5) was repeated. The powders, after drying at 100 °C, were calcined for 3 h at 700 °C. Mn was loaded in TiO_2 with molar ratio in different concentrations between 0 and 1 wt%.

Furthermore, samples of calcareous filler containing 0%, 5% or 10% of the 0.1% Mn:TiO_2 photocatalyst were deposited on 0.25 m × 0.25 m glass panels.

2.2. Photocatalytic experiments

Photocatalytic degradation of MB ($C_{16}H_{18}ClN_3S$) in aqueous solution (10 mg L^{-1}) was carried out under UV (310–400 nm wavelength) using a mercury Lamp (Spectroline ultraviolet quartz pencil lamp/I = 4.5 mW cm^{-2}) and visible-light (Osram Dulux, 11 W) irradiation. About 100 mg of photocatalyst was added into a 100 ml of aqueous MB (10 ppm) solution. Prior to irradiation, the suspensions were sonicated in the dark for 30 min to ensure establishment of an adsorption–desorption equilibrium among the photocatalyst, MB and atmospheric oxygen. After recovering the catalyst by centrifuging, subsequent variations in the MB concentration were analyzed by an Ultraviolet–visible spectrophotometer (VARIAN Cary 50) and the adsorption peak at 664 nm (λ_{max} for MB) was recorded.

The photocatalytic activity of calcareous paint (containing 5% and 10% of the 0.1 wt% of Mn:TiO_2) was examined employing a photocatalytic system which was comprised of a gas delivery unit, a reactor chamber and a measurement unit (Fig. 2). A compressed gas cylinder of 10 ppmv NO (±2%) balanced in N_2 was used for the creation of NO_x polluted atmosphere in the photocatalytic reactor (Linde Hellas Ltd.). Prior to its introduction to the photocatalytic chamber, NO was mixed with the appropriate quantity of synthetic air (20.5% v/v O_2 and 79.5% v/v N_2) adjusting the initial NO_x concentration to $C_{NO} = 250\ \mu g\ m^{-3}$.

Photocatalytic experiments were carried out in a cubic pyrex glass reaction chamber of 0.125 m^3 volume capacity (50 cm × 50 cm × 50 cm) which was placed inside a (light) sealed irradiation box. The photocatalytic films were placed at the bottom surface of the cell. The cell's loading factor l_f (photocatalyst surface/cell volume ratio) was estimated to be about 0.442 $m^2\ m^{-3}$.

Illumination was provided by ten 15 W Philips TLD 15 W/08 fluorescent black light blue type, or ten vis lamps (PHILIPS $FSL_{YZ15RR26}$) being placed horizontally in pairs on each side of the irradiation box at a distance of approximately ∼20 cm from the photocatalytic material. The total light intensity measured on the samples' surface by the ten TLD lamps was on average 2.6 W m^{-2}, of which 55% (1.43 W m^{-2}) was due to UV. The corresponding total light intensity value for the 10 FSL lamps (vis) was 7.6 W m^{-2}, of which only the 0.6% was attributed to UV. The irradiation time was set in 45 min. The environmental box was also further equipped with two fans for keeping the temperature stable.

The initial concentration of the air pollutant as well as the adopted temperature and humidity levels into the inner environment of (inside) the glass cell were chosen with the ultimate criterion of approaching the corresponding levels of the same variables in the outdoor real environment. For that purpose the NO concentration was established at approximately 250 $\mu g\ m^{-3}$, while the temperature and humidity levels were controlled at 24–27 °C and 35–45% respectively. The NO_x concentration was measured with a chemiluminescence NO_x analyzer (Environment S.A AC42M) which was connected in line to the outlet of the reactor.

2.3. Characterization of manganese-doped TiO_2 nanoparticles

The crystal structure, particle size, morphology, and porosity were examined with an XRD-powder system, SEM, TEM and