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Low-temperature synthesis and characterization of rutile nanoparticles with amorphous surface layer for photocatalytic degradation of caffeine

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ABSTRACT

Rutile (TiO_2) nanoparticles were prepared by a low-temperature hydrothermal process from titanium(IV) isopropoxide as a precursor and without any additional calcination step. The particles were characterized with several techniques (XRD, BET, UV–vis spectrometry, TEM/HRTEM/SAED, FT-IR) and their photocatalytic efficiency was evaluated on the degradation of caffeine. The as-prepared rutile particles exhibited a rod-like morphology with a prism body and pyramidal ends. The low-temperature hydrothermal synthesis introduced an amorphous layer that was around 1-nm thick and uniformly covered the surfaces of the particles. The enhanced photocatalytic properties of the particles confirmed the positive impact of the amorphous surface layer in comparison to the fully crystallized surface of commercial rutile particles and to particles that were synthesized using a conventional high-temperature calcination route. The amorphous surface layer seems to enhance the adsorption of both oxygen and caffeine on the surface of the particles and, therefore, improves the photocatalytic activity of the rutile particles. Being the case, the electron transfer to the adsorbed oxygen is more efficient, increasing the life-time of the photogenerated holes, which contributes to the degradation of caffeine via the formation of reactive radicals and/or by direct oxidation.

1. Introduction

In recent years, the remediation of hazardous wastes, contaminated groundwaters and toxic air has attracted the attention of scientists all over the world. In order to overcome this problem, extensive research is being conducted to develop new methods for the characterization and elimination of hazardous chemicals from air, soil and water [1].

Semiconductor photocatalysis is a physicochemical method that exploits the characteristic electronic structure of the material and is able to directly or indirectly enhance the oxidation of different pollutants [1].

TiO_2 is known to be the most promising material for semiconductor photocatalysis, not only because of its adequate band-gap energy and thermodynamics of the valence and conduction bands, but also because of the chemical properties of the surface, which play a major role in the photocatalytic process [2].

Photocatalysis has been extensively investigated on two crystal modifications of TiO_2: anatase and rutile. Rutile has shown much lower photocatalytic activity than anatase in all types of reaction media and in the presence of oxygen gas [2]. There are various properties that can explain the superiority of anatase over the rutile phase in terms of photocatalysis. The first one is the electron–hole recombination: rutile has a smaller band-gap than anatase, which means that excited electrons recombine with photogenerated holes faster and, therefore, do not participate in the photocatalytic reaction [3]. The second one is the hydroxylation degree of the adsorbed surface: rutile is normally obtained at high temperatures, which induces irreversible dehydroxylation of the surface and reduces the photocatalytic properties [2,4], while the surface of anatase is commonly highly hydroxylated and, therefore, oxygen and water molecules can adsorb on its surface and initiate the photocatalytic reaction. The next important feature is the particle size: smaller particles have higher specific surface areas. Rutile is thermodynamically the most stable crystalline form at all temperatures and is particularly stable for particles larger than 35 nm, while for

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particles smaller than 11 nm the metastable anatase form dominates; therefore, the size alone provides a good explanation for the better photocatalytic activity of the anatase phase [5]. The reality, however, is not so straightforward: smaller particles usually have a lower crystallinity and therefore a larger number of defects that enhance the recombination of the electron/hole pairs. Furthermore, below a certain size there is an inversion on the band gap energy, increasing it, which lowers their photocatalytic activity [5–7].

On the basis of the described the rutile phase has been regarded as the less-favorable modification of TiO_2 in terms of photocatalytic activity. Nevertheless, rutile particles have an advantage in terms of their activation energy: the smaller band-gap (3.0 eV) of the material enables the use of visible-light illumination, which can be a major factor in the synthesis of photocatalytic materials. The traditional preparation method for rutile particles is the high-temperature calcination of anatase particles that transforms the anatase to rutile above 600 °C [8]. This calcination treatment greatly affects the surface and the size of the particles; therefore, a low-temperature synthesis would be a reasonable solution in order to obtain improved photocatalytic properties for the rutile particles.

In this work the rutile particles were prepared on a two-step synthetic procedure: the first step was the well-established formation of a peroxotitanium complex between hydrogen peroxide molecules and Ti^{4+} ions [9]. The procedure was additionally upgraded with a hydrothermal treatment, in a second step. Both procedures were conducted at low-temperatures and the particles were not thermally treated at the end of the synthesis. The photocatalytic activity of the prepared samples was evaluated on the degradation of caffeine. This compound was chosen as a model degradation molecule for different reasons: it is the origin of domestic sanitary contamination and the mechanism of its degradation has been already investigated in an aqueous suspension of TiO_2 particles [10,11]. The structural and photocatalytical properties of the as-prepared particles were compared with two commercial rutile particles and also with rutile particles synthesized using the traditional high-temperature method. The influence of the structure of the surface on the photocatalytic efficiency is discussed and explained.

2. Materials and methods

2.1. Chemicals

Titanium(IV) isopropoxide (TIP: $Ti(OCH(CH_3)_2)_4$, Acros Organics, New Jersey, USA), hydrogen peroxide (H_2O_2, 35 wt.%, Acros Organics, New Jersey, USA), isopropanol ($CH_3CH(OH)CH_3$, AppliChem GmbH, Darmstadt, Germany), nitric acid (HNO_3, 65%, AppliChem GmbH, Darmstadt, Germany) and caffeine (≥99.0% HPLC grade, Sigma–Aldrich Chemie GmbH, Steinheim, Germany) were used without further purification.

2.2. Samples preparation

TiO_2 nanoparticles were prepared in a two-step synthesis procedure. In the first step, TIP diluted with isopropanol was added dropwise to an aqueous solution of H_2O_2 under vigorous stirring. A molar ratio $[H_2O_2]$: [Ti] of 20 was used for a Ti concentration of 0.158 M at pH of 0.5 adjusted with HNO_3, according to Zhang et al. [9]. The red solution was cooled with ice until the particles started to precipitate. The resulting orange suspension was further treated at 70 °C under reflux conditions for 24 h.

In the second step (hydrothermal treatment), 50 mL of reflux suspension was put inside a Teflon-lined stainless-steel autoclave (50% filling). The autoclave was placed inside a heating chamber with mechanical convection (Binder FED 53) and set to 75 °C for 8, 24 and 96 h (HT8, HT24, HT96). The precipitate was washed with de-ionized water three times and dried at room temperature.

As-prepared samples were compared with three rutile powders: commercial rutile Tronox (C1, Tronox Incorporated, Oklahoma City, USA), rutile particles from Cinkarna Celje (C2, Cinkarna Celje d.d., Celje, Slovenia) and a third sample prepared with the sol–gel synthesis of the anatase phase from a TIP precursor and the traditional conversion to the rutile phase at 800 °C (T800).

2.3. Materials characterization

The phases in the samples were characterized by powder X-ray diffraction (XRD) using a PANalytical X'Pert PRO diffractometer.

The specific surface area measurements (BET) were conducted using a Micromeritics Gemini II 2370 Surface Area Analyzer.

An FT-IR spectrophotometer (PerkinElmer Spectrum 100 FT-IR) equipped with TGS detector and an ATR (attenuated total reflection) module was used for the surface characterization of the TiO_2 particles. The TiO_2 powder was pressed on the ATR window (d = 2 mm) and the spectra were collected from 4 scans, each with a nominal resolution of 2 cm^{-1}. The background was measured with the ATR module without any sample.

The diffuse-reflectance UV–vis spectra of the photocatalysts were measured on a JASCO V-560 UV-Vis spectrophotometer equipped with an integrating sphere (JASCO ISV-469). $BaSO_4$ powder was used as a reference to provide a 100% reflectance measurement. The spectra were recorded in the diffuse reflectance mode and transformed by the instrument software (JASCO) to equivalent absorption Kubelka–Munk units and then the band-gap values were determined.

The particles were investigated with a JEOL 2010F transmission electron microscope equipped with a field emission gun. The microscope was operated at 200 kV.

2.4. Photocatalytic experiments

The photocatalytic activities of the TiO_2 powder samples were investigated by measuring the degradation of a 50 mg L^{-1} caffeine solution under UV/vis illumination source (Heraeus TQ 150 medium-pressure mercury-vapor lamp), in a setup described elsewhere [12]. A DURAN® glass cooling jacket was used to obtain irradiation in the near-UV to visible light range ($\lambda > 350$ nm; main emission lines at 366, 436 and 546 nm). The photon flow entering the reactor was determined with an Ocean Optics spectroradiometer positioned in the photoreactor, i.e. 4 cm away from the lamp, the total irradiance at this point being equal to 27 mW cm^{-2}. In a typical experiment, 7.5 mg of a TiO_2 sample was mixed with 7.5 mL of the caffeine aqueous solution inside a 10-mL quartz reactor. The reaction was performed in the presence of oxygen or argon flow as well as under natural dissolved oxygen, separately. The suspension was firstly stirred for 30 min in the dark to achieve the absorption–desorption equilibrium of caffeine on the surface of the particles. Afterwards, the reactor was exposed to the illumination source (t = 0 min for reaction) and samples were taken from it during different periods of the reaction. The concentration of caffeine was monitored by a high-performance liquid chromatography apparatus (Hitachi Elite LaChrom) equipped with a diode array detector (L-2450) and a solvent delivery pump (L-2130). A gradient method at a constant flow rate of 1 mL min^{-1} was used in a Purospher Star RP-18 column (250 mm × 4.6 mm; 5 μm particles). First, the column was equilibrated with a A:B (70:30) mixture of milli-Q water (A) and methanol (B), followed by a linear gradient run to A:B (20:80) in 30 min and finally with isocratic elution over a period of 2 min.