



Photocatalytic degradation of alprazolam in water suspension of brookite type TiO₂ nanopowders prepared using hydrothermal route

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H I G H L I G H T S

- Brookite-type TiO₂ powders synthesized by combined sol–gel–hydrothermal method.
- Powders investigated by XRD, SEM, EDS, BET, SE and Raman spectroscopy.
- Photocatalytic degradation of alprazolam under UV radiation.
- Photocatalytic activity attributed to high content of brookite phase.
- High photocatalytic efficiency of pure brookite sample, comparable to Degussa P25.

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Two series of nanocrystalline brookite-type powders have been synthesized by using combined sol–gel–hydrothermal method with titanium tetrachloride (TiCl₄) as a precursor and hydrothermal temperature and reaction time varied in the range of 120–200 °C and 12–48 h, respectively. The effects of chosen synthesis parameters on structural, morphological and optical properties of synthesized powders have been investigated by the XRPD, SEM, EDS and BET measurements, as well Raman spectroscopy and spectroscopic ellipsometry. The XRPD results have shown that pure brookite phase, with mean crystallite size of ~33 nm, has been obtained only in the sample synthesized at 200 °C, after 24 h of hydrothermal process. In all other samples anatase phase also appears, whereas rutile and sodium titanate phases have been noticed in the samples synthesized at lower temperatures. The presence of different titania phases has also been confirmed and analyzed by Raman scattering measurements. The SEM measurements have shown spindle-like particles in brookite-rich samples synthesized at 200 °C, whereas BET measurements have detected mesoporous structure in these samples. The properties of synthesized powders have been correlated to their photocatalytic efficiency, tested in degradation of alprazolam, one of the 5th generation benzodiazepines. The sample consisted of pure brookite has shown the highest efficiency in the photodegradation of alprazolam, practically equal to the activity of Degussa P25.

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1. Introduction

Titanium dioxide (titania, TiO₂) is known as a polymorphic

material with three naturally occurring crystalline modifications: anatase, rutile and brookite. These structures are composed of TiO₆ octahedra, with edge and corner sharing organized in a different way, which is also characteristic of various titanate materials [1–4]. Brookite is the rarest of the natural TiO₂ polymorphs. As opposite to anatase and rutile, common titania polymorphs easily synthesized by a variety of techniques from different titanium compounds, the

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brookite occasionally appears as a by-product obtained together with either anatase or rutile or both of these phases. Consequently, the brookite has been much less characterized phase in comparison to anatase and rutile [2,5]. The investigation of properties and potential applications has been limited due to difficulties in synthesis of pure brookite phase [2,6–11], related mainly to narrow range of synthesis conditions, which allow brookite phase to be produced [5,12]. However, the interest in brookite has been increased in recent years and pure brookite has been observed as an interesting candidate in photocatalytic applications [5,13–15].

Titania may be generally obtained by thermolysis, hydrothermal synthesis and sol–gel process [10]. Well-crystallized titania nanoparticles have been produced by using hydrothermal method [6], which has been proven as necessary in synthesizing brookite as major phase [10]. Since this treatment with titanium tetrachloride as a precursor and the addition of NaOH into reaction solution can lead to all three polymorphs of titania, the control of synthesis parameters, such as hydrothermal temperature [16] and reaction time [14] is of a great importance. Also, under these hydrothermal conditions, certain solution pH (high basicity) and particular amounts of Na cations are necessary to produce pure brookite phase [2,4,17] (and references therein). Therefore brookite type nanopowders, investigated in this study, have been prepared by combined sol–gel–hydrothermal method with TiCl_4 as a precursor, in alkaline environment, with hydrothermal temperature and time varied. The effects of chosen synthesis parameters on the crystallite size, structure and phase composition of the synthesized nanopowders have been investigated by X-ray powder diffraction (XRPD), energy-dispersive X-ray spectroscopy (EDS), and Raman scattering measurements. The morphological properties of samples have been studied by scanning electron microscopy (SEM) and the Brunauer–Emmett–Teller (BET), whereas their optical properties have been investigated by the spectroscopic ellipsometry (SE) measurements.

The properties of synthesized brookite-type titania nanopowders have been correlated to their photocatalytic efficiency, tested in degradation of alprazolam and compared to the efficiency of commercial Degussa P25 under the same conditions. Alprazolam is one of the 5th generation benzodiazepines [18,19], a group of psychiatric substances acting on the central nervous system [19–21] and, similarly to the other pharmacological groups, occurring in the environment in the range of ng/l – $\mu\text{g/l}$ [22]. The presence of these compounds in the ecosystems might have a significant effect on non-target organisms [23]. In the research investigating the stability of the benzodiazepines under the influence of simulated solar irradiation, only alprazolam has shown high resistance to photodegradation [24]. Having in mind continuous input of this kind of pharmaceuticals in the environment and their persistence, there is a great interest to find new methods for their removal.

2. Experimental

2.1. Synthesis of brookite-type powders

Brookite type nanoparticles have been prepared by using combined sol–gel–hydrothermal method with TiCl_4 (99.0% pure, Merck) as a precursor. An appropriate amount of TiCl_4 has been dissolved in 150 ml of distilled water under vigorous stirring on the ice-bath. In order to obtain the hydrogel, the aqueous solution of NaOH has been added under careful control of the pH value of the solution (9.3). After aging in the mother liquor for 5 h, as-prepared hydrogel has been placed in a steel pressure vessel (autoclave) under a controlled temperature. After treatment, filtration and washing with distilled water until complete removal of chloride

ions, were carried out. The last step was drying at 105.5°C for 72 h. Two series of samples have been produced by varying the hydrothermal temperature and reaction time. In the first series the reaction time was 24 h at different temperatures: 120, 160, and 200°C . The second series of samples was prepared by keeping the temperature at 200°C , while the time of treatment was 12, 24, and 48 h. The labels assigned to samples, concerning the hydrothermal temperature and reaction time are listed in Table 1.

2.2. Characterization methods

The X-ray powder analysis was used to identify the crystalline phases, as well as to calculate lattice parameters of brookite phase in synthesized powders. The XRPD patterns of all samples were recorded on Rigaku (Ultima IV) X-ray Powder Diffractometer with $\text{Cu K}\alpha_{1,2}$ radiation ($\lambda = 1.54178 \text{ \AA}$). The measurements were performed in the 2θ range from 10° to 80° with the step of 0.02° and scanning time of 2 s/min. The calculation of the volume-weighted mean crystallite size (D) was performed on the basis of the full width at half maximum intensity of the all reflections for brookite phase by using Scherrer's formula [25].

Morphology of the synthesized nanopowders has been studied on SEM type JEOL JSM-6460LV with the operating voltage of 20 keV. The composition/quality has also been analyzed by using the same SEM instrument equipped with an EDS INCAx-sight detector and “INAX-stream” pulse processor (Oxford Instruments).

Adsorption–desorption isotherms were obtained by nitrogen adsorption at 77 K using a Sorptomatic 1990 Thermo Finnigan device. Prior to adsorption, the samples were outgassed for 1 h under vacuum at room temperature and, additionally, at 110°C and the same residual pressure, for 16 h. The specific surface areas (S_{BET}) of samples is calculated from the linear part of the adsorption isotherm by applying the Brunauer–Emmet–Teller (BET) equation [26]. The total pore volumes (V_{tot}) were obtained from the N_2 adsorption, expressed in liquid form, by using the Gurvitsch rule [27]. The micropore volume (V_{mic}) has been estimated by the Dubinin–Radushkevich method [28]. The mesopore volume (V_{mes}), as well as mesopore size distribution have been estimated by the Barrett, Joyner and Halenda (BJH) method from the desorption branch of the isotherms [29].

The Raman scattering measurements on brookite-type powders pressed into pellets were performed using a TriVista TR557 triple spectrometer with the 900/900/1800 grooves/mm gratings combination, equipped with a nitrogen-cooled charge coupled device (CCD) detector. All spectra have been collected in backscattering micro-Raman configuration at room temperature in the air. The 488 nm line of a mixed Ar^+/Kr^+ gas laser was used as an excitation source with an output power of less than 10 mW to avoid local heating due to laser irradiation.

The ellipsometric spectra of the brookite-type nanopowders have been measured by SOPRA GES-5 variable angle ellipsometer in rotating polarizer configuration. The data were collected at room temperature, in the range from 1.5 to 6.2 eV with resolution of 0.04 eV and incidence angle of 65° .

3. Photocatalytic measurements

The photocatalytic activity of the nanopowders was evaluated

Table 1
The parameters of hydrothermal synthesis.

	B _{120/24}	B _{160/24}	B _{200/24}	B _{200/12}	B _{200/48}
Treatment temperature ($^\circ\text{C}$)	120	160	200	200	200
Hydrothermal reaction time (h)	24	24	24	12	48

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