



Brookite TiO₂-based materials: Synthesis and photocatalytic performance in oxidation of methyl orange and As(III) in aqueous suspensions



M.J. López-Muñoz*, A. Revilla, G. Alcalde

Department of Chemical and Environmental Technology, ESCET, Universidad Rey Juan Carlos, C/ Tulipán s/n, 28933 Móstoles, Madrid, Spain

ARTICLE INFO

Article history:

Received 20 January 2014

Received in revised form 16 April 2014

Accepted 14 May 2014

Available online 29 June 2014

Keywords:

Brookite
Titanium dioxide
Photocatalysis
Arsenic oxidation
Methyl orange

ABSTRACT

A series of titania samples consisting of pure brookite, brookite/anatase and brookite/layered titanate hybrids were synthesized by a hydrothermal method. The influence of experimental variables, including electrolyte concentration, temperature and duration of hydrothermal treatment, on structural and physical properties of the resulting materials was investigated. The crystalline phase composition of the materials was analyzed by X-ray diffraction, the morphology was examined by scanning electron microscopy (SEM) and the specific surface areas were measured according to the Brunauer–Emmett–Teller method. Pure brookite could be obtained by hydrothermal treatment at 180 °C with addition of 0.25 M NaCl, 0.5 M NaCl or 0.1 M NaOH, and adjustment of reaction time. Brookite samples prepared by addition of NaCl as source of Na⁺ ions showed a flower-type morphology, whereas those synthesized with NaOH consisted in micrometric-size aggregations of nanoparticles. The photocatalytic activity of the materials was evaluated by means of methyl orange bleaching and by As(III) to As(V) oxidation.

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1. Introduction

Titanium dioxide is a semiconductor most widely used in photocatalytic processes applied to the treatment of toxic and refractory pollutants in aqueous solutions. TiO₂ can crystallize in different polymorphs: rutile (tetragonal, space group *P4₂/mnm*), anatase (tetragonal, space group *I4₁/amd*) and brookite (orthorhombic, space group *Pbca*) [1]. The three crystal structures are made up of distorted TiO₆ octahedra linked by shared edges and/or corners in different ways that give rise to different electronic and surface properties. Among the natural TiO₂ polymorphs, brookite is the rarest and the most difficult phase to prepare in the laboratory, as the experimental conditions that can guarantee both selective nanocrystal nucleation and growth in this crystal phase are inherently the most restrictive [2]. As a consequence, the properties of brookite, either pure or coupled with other titania phases, have been much less studied in comparison to those of anatase or rutile and therefore the potential of brookite for photocatalytic applications is poorly known.

Different strategies have been described in the literature for the synthesis of brookite particles. Most of them are based on hydrothermal methods either in aqueous or organic media using a variety of precursors such as titanium alcoxides, TiCl₄ or titanium-containing organic complexes, among others [2–8]. Independent of the synthesis method, it was generally reported that a precise adjustment of reaction variables was needed to yield pure brookite; otherwise, the resulting materials consisted in a mixture of brookite with titanate and/or anatase phase. The photocatalytic activity associated to brookite phase is, however, still controversial. Lin et al. [3] found that flower- and spindle-like brookite did not show any catalytic activity toward methyl orange decomposition, whereas brookite nanosheets possessing a similar specific surface area and absorption edge as the nanospindles showed an activity higher than Degussa P25 TiO₂. By contrast, Zhao et al. [4] reported that brookite nanoflowers prepared by an alkaline hydrothermal method had a photocatalytic activity per surface area higher than anatase for methyl orange decomposition. On the other hand, some authors report that brookite–anatase mixture materials can exhibit high photocatalytic performances attributed to a synergistic interaction between both TiO₂ polymorphs, though this effect is not always observed [4,5,9,10].

In the present work, a series of samples with different brookite contents were synthesized following an alkaline hydrothermal

* Corresponding author. Tel.: +34 916647464; fax: +34 914887068.
E-mail address: mariajose.lopez@urjc.es (M.J. López-Muñoz).

Table 1
Synthesis conditions, phase composition, crystallite size of brookite and specific surface area of TiO₂ samples.

Sample	Electrolyte	T of hydrothermal treatment (°C)	Time of hydrothermal treatment (h)	Phase composition ^a	Crystal size of brookite (nm)	S _{BET} (m ² g ⁻¹)
L1_24	NaCl, 0.1 M	170	24	B+LT	–	217.2
L2_24	NaCl, 0.25 M	170	24	LT	–	236.3
L5_24	NaCl, 0.5 M	170	24	LT	–	214.8
L1_48	NaCl, 0.1 M	170	48	A+B+LT	50.7	114.1
L2_48	NaCl, 0.25 M	170	48	B+LT	73.2	63.0
L5_48	NaCl, 0.5 M	170	48	B+LT	–	143.7
L2_72	NaCl, 0.25 M	170	72	B+LT	86.0	73.6
L5_72	NaCl, 0.5 M	170	72	B+LT	50.5	156.2
H.72	None	180	72	A	–	28.7
H1_24	NaCl, 0.1 M	180	24	A+B	45.8	72.1
H2_24	NaCl, 0.25 M	180	24	B+LT	72.9	181.0
H5_24	NaCl, 0.5 M	180	24	LT	–	213.0
H1_48	NaCl, 0.1 M	180	48	A+B	38.6	63.3
H2_48	NaCl, 0.25 M	180	48	B	73.2	24.8
H1_72	NaCl, 0.1 M	180	72	A+B	37.9	27.0
H2_72	NaCl, 0.25 M	180	72	B	46.2	25.1
H5_72	NaCl, 0.5 M	180	72	B+LT	103.8	160.0
H5_192	NaCl, 0.5 M	180	192	B	181.6	23.6
Na ₂ CO ₃ _H1_24	Na ₂ CO ₃ , 0.1 M	180	24	A+B	38.6	55.2
Na ₂ CO ₃ _H1_72	Na ₂ CO ₃ , 0.1 M	180	72	A+B	73.2	22.7
NaOH.H1_24	NaOH, 0.1 M	180	24	B+LT	38.6	65.7
NaOH.H1_72	NaOH, 0.1 M	180	72	B	104.3	51.7

^a A: anatase; B: brookite; LT: layered titanates.

method. The influence of experimental variables, such as the source of electrolyte, electrolyte concentration, temperature and duration of hydrothermal treatment, on the crystalline phase composition and physical properties of the resulting materials was investigated. The activity of brookite materials as photocatalysts was subsequently evaluated by two processes: the degradation of methyl orange (MO) organic molecule is widely taken as a model compound in photocatalytic studies, and the oxidation of inorganic species As(III) (arsenite) to As(V) (arsenate). The latter process is nowadays required for most treatment technologies to remove arsenic from water because of the lesser mobility and toxicity of arsenate in comparison to arsenite species [11,12].

2. Experimental

2.1. Synthesis of TiO₂ materials

The synthesis of materials was performed following a hydrothermal method based in that reported by Zhao et al. [4]. In a typical procedure, 15.6 ml of titanium *n*-butoxide (TNB) (97%, Aldrich) was hydrolyzed in 136 ml of NH₃ (32%, Scharlau) aqueous solution and sodium chloride (NaCl) (99%, Scharlau). The concentration of NaCl in the total volume of solution was varied in the range 0–0.5 M. The resulting suspensions were transferred to a Teflon-lined autoclave and heated to either 170 or 180 °C for different times (24–192 h range). The powders obtained were washed with deionized water and dried at 110 °C overnight.

Hereafter, the samples will be denoted as L_x.*t* or H_x.*t*, where L or H indicates the temperature of the hydrothermal treatment (170 or 180 °C, respectively), *x* stands for the electrolyte concentration (1, 2 or 5 for 0.1, 0.25 and 0.5 M, respectively) and *t* indicates the duration of the treatment in hours. A series of samples were also obtained by replacing NaCl for Na₂CO₃ (>99%, Acros) or NaOH (98%, Scharlau), respectively, named as Na₂CO₃_H1_24, Na₂CO₃_H1_72, NaOH.H1_24 and NaOH.H1_72. The synthesis conditions for all materials are summarized in Table 1.

2.2. Photocatalyst characterization

The crystalline phases of the catalysts were investigated by powder X-ray diffraction (XRD). Diffraction patterns were obtained

on a Philips X-PERT MPD diffractometer using Cu K α radiation as the X-ray source. The morphology of the solids was examined by scanning electron microscopy (SEM) using a XL30 ESEM Philips equipment and Nova Nano SEM230 (FEG-SEM). TEM images were acquired in a PHILIPS TECHNAI 20T electron microscope operating at 200 kV and with a 2.7 Å resolution. Samples were prepared by dispersing a small amount in acetone and adding a droplet of the suspension onto a carbon-coated copper grid. The surface area (S_{BET}) measurements were carried out according to the Brunauer–Emmett–Teller (BET) method determined by nitrogen adsorption–desorption isotherms at 77 K on a Micromeritics Tristar 3000 instrument.

2.3. Photocatalysis procedure

The photocatalytic reactions were performed in a batch Pyrex reactor of 1 l effective solution volume. Reaction mixtures containing either methyl orange (MO; C₁₄H₁₄N₃SO₃Na 85%, Aldrich) or As(III) (NaAsO₂ 90%, Aldrich) with an initial concentration of 30 mg l⁻¹ were prepared with deionized water (Milli-Q). The runs were carried out at the natural pH values of the solutions, i.e., 7.5 for MO and 9.2 for As(III).

Irradiations were carried out using a 150 W medium-pressure mercury lamp (Heraeus TQ-150), placed inside a Pyrex jacket and provided with a cooling tube through which an aqueous solution of copper sulfate (0.01 M) was circulated to prevent the overheating of the suspension and to cut off the radiation below 300 nm. The catalyst loading was fixed at 1 g l⁻¹. Prior to irradiation, the suspensions were kept in the dark for 60 min to achieve adsorption/desorption equilibrium. Continuous air bubbling and stirring were maintained through the reaction. At given time intervals, aliquots were taken and subsequently filtered through 0.22 μm of cellulose filters to separate the suspended catalyst particles before being analyzed.

2.4. Analysis

The progress of photocatalytic reactions was monitored using a UV–visible spectrometer (JASCO V-630). The concentration of methyl orange was measured from the absorbance at the wavelength of 462 nm by using a calibration curve.

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