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Photocatalytic behavior of TiO_2 films synthesized by microwave irradiation

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ABSTRACT

Titanium dioxide was synthesized on glass substrates from titanium (IV)isopropoxide and hydrochloride acid aqueous solutions through microwave irradiation using as seed layer either fluorine-doped crystalline tin oxide (SnO_2:F) or amorphous tin oxide (a-SnO_x). Three routes have been followed with distinct outcome: (i) equimolar hydrochloride acid/water proportions (1_{HCl}:1_{water}) resulted in nanorod arrays for both seed layers; (ii) higher water proportion (1_{HCl}:3_{water}) originated denser films with growth yield dependent on the seed layer employed; while (iii) higher acid proportion (3_{HCl}:1_{water}) hindered the formation of TiO_2. X-ray diffraction (XRD) showed that the materials crystallized with the rutile structure, possibly with minute fractions of brookite and/or anatase. XRD peak inversions observed for the materials synthesized on crystalline seeds pointed to preferred crystallographic orientation. Electron diffraction showed that the especially strong XRD peak inversions observed for TiO_2 grown from the 1_{HCl}:3_{water} solution on SnO_2:F originated from a [001] fiber texture. Transmittance spectrophotometry showed that the materials with finer structure exhibited significantly higher optical band gaps. Photocatalytic activity was assessed from methylene blue degradation, with the 1_{HCl}:3_{water} SnO_2:F material showing remarkable degradability performance, attributed to a higher exposure of (001) facets, together with stability and reusability.

1. Introduction

Titanium dioxide (TiO_2) is non-toxic, chemically stable, earth-abundant and shows remarkable photocatalytic activity in the decomposition of organic pollutants [1–6]. TiO_2 exists in amorphous form or in three different crystalline structures: rutile, anatase or brookite [7]. Typically, either rutile and/or anatase are used for photocatalysis [8].

Photocatalytic degradation is based on redox reactions occurring on the semiconductor oxide surface; when TiO_2 absorbs photons with energy greater than its band gap (respectively, 3.0 eV for rutile and 3.2 eV for anatase [7]) electrons are excited from the valence band to the conduction band, creating electron–hole pairs [9] that diffuse in their respective band to the TiO_2 surface, oxidizing adsorbed chemical compounds [10]. This activity depends on the crystalline structure, crystal size, type and proportion of impurities present, specific surface area and exposed crystallographic facets [4].

In degradation processes, TiO_2 is usually employed in the form of powder or film. However, powder involves expensive steps in photocatalyst recycling [11] and full separation may be difficult to achieve [1]. Nanostructuring has been reported to improve the photocatalytic performance of films [4], and one-dimensional structures, such as nanorods arrays, have been proposed to offer advantages due to the high surface/volume ratio, which results in high density of active sites for surface reactions and high interfacial charge carrier transfer rates [12,13].

Several synthesis routes can be employed in the production of TiO_2 films and nanorod arrays, ranging from template-assisted approaches and sputtering [2] to conventional hydrothermal synthesis [14–17]. Nevertheless, the latter method is usually slow [18]

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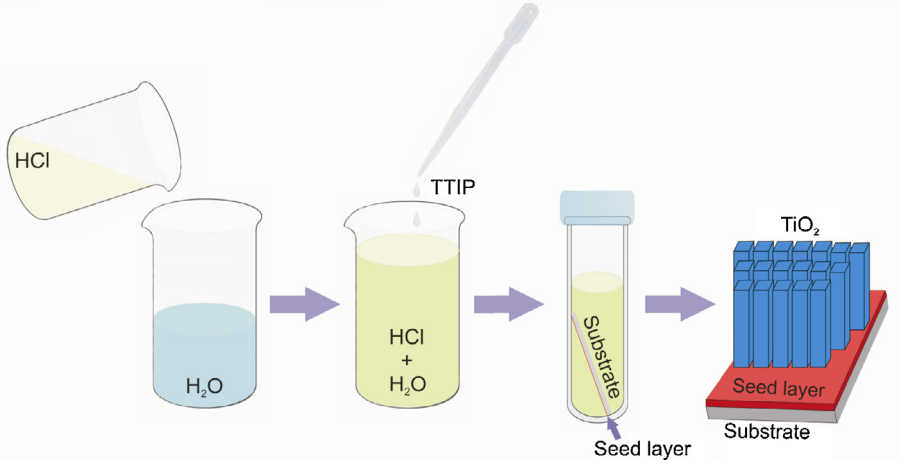

Fig. 1. Scheme of the TiO_2 synthesis procedure.

and microwave-assisted synthesis appears as a viable alternative due to increased growth rates [18], high efficiency/cost relation [19,20] and enhanced uniformity [18].

The present work reports the effect of a systematic variation of solution composition and type of seed on the photocatalytic activity of nanostructured TiO_2 materials synthesized by a microwave-assisted hydrothermal method. Structural characterization has been carried out by X-ray diffraction (XRD), scanning electron microscopy (SEM) coupled with both energy dispersive X-ray spectroscopy (EDS) and electron backscatter diffraction (EBSD), and transmission electron microscopy (TEM) in association with selected area electron diffraction (SAED). Optical properties have been investigated through transmittance spectrophotometry and photoluminescence, while the photocatalytic activity has been assessed from the evolution of methylene blue (MB) concentration in organic pollution surrogate solutions. MB was considered as a model-test contaminant and indicator due to its photocatalytic activity and absorption peaks in the visible range, thus its degradation can be easily monitored by optical absorption spectroscopy [21].

2. Experimental

2.1. Nanostructured TiO_2 production

Different synthesis strategies have been tested involving (i) two types of seed layers, amorphous or crystalline tin oxide; and (ii) starting solutions containing 3.33% vol. of titanium (IV)isopropoxide 97% (TTIP from Sigma–Aldrich) with three different water/hydrochloride acid volume proportions, 1_{HCl}:1_{water}, 1_{HCl}:3_{water} and 3_{HCl}:1_{water}.

Previous work showed that direct growth of TiO_2 on glass results in unlike outcomes, in some cases without the formation of film [22,23]. Since rutile presents a small lattice mismatch with the isostructural SnO_2, in the present study commercial fluorine-doped tin oxide (SnO_2:F) has been used as crystalline seed (SnO_2:F coated glass with a surface resistivity of 7 Ω/sq, from Sigma–Aldrich). The amorphous SnO_x layers (a-SnO_x) were deposited on glass by reactive radio frequency (rf) sputtering at room temperature and annealed at T = 150 °C for 1 h. Deposition was carried out using an AJA Orion rf magnetron sputtering system with a Sn target in O_2/Ar atmosphere with flow of 9/18 SCCM and rf power of 40 W.

Immediately prior to the synthesis process, HCl was stirred with water for 5 min, the Ti precursor was added and the solutions were stirred for 10 min (see scheme in Fig. 1). Microwave irradiation was performed using a CEM Focused Microwave Synthesis System Discover SP. Time, power and maximum pressure have been set at 75 min, 100 W and 17 bar, respectively. Solution volumes of 20 ml were transferred into capped quartz vessels of 35 ml, which were kept sealed by the constraining surrounding pressure. Under these conditions the reaction temperatures remained around 110 °C for the 1_{HCl}:1_{water} conditions and at 100 °C in the other cases. For each synthesis, a piece of seeded glass of 15.0 mm × 30.0 mm × 2.3 mm, ultrasonically cleaned in acetone (10 min) and isopropanol (10 min), was placed at an angle against the vessel with the seed layer facing down (Fig. 1) [22]. After the synthesis process, the materials were cleaned with deionized water and dried with nitrogen.

2.2. Diffraction and microscopy

X-ray diffraction measurements were performed both in Bragg–Brentano configuration and in parallel beam grazing-incidence (GIXRD) with a PANalytical's X'Pert PRO MPD diffractometer using CuKα radiation. The Bragg–Brentano XRD data were acquired in the 20–72° 2θ range with a step size of 0.016° using an X'Celerator 1D detector. The GIXRD data were recorded with the detector rotated to a 0D configuration and at incidence angles of 0.5, 0.75 and 1° with a rotation step size of 0.1°. For comparison, powder diffractograms of rutile, anatase, brookite have been simulated with PowderCell [24] using crystallographic data from Ref. [25]. The SnO_2 powder diffractogram was also simulated to identify peaks originating from the seed layer.

Surface and cross-section SEM observations were carried out using a Carl Zeiss AURIGA CrossBeam FIB-SEM workstation equipped for EDS and EBSD measurements. The thickness of the films and dimensions of individual nanorods have been determined from SEM micrographs using the ImageJ software [26]. For EBSD analysis, the films were scratched and the resulting power dispersed in isopropyl alcohol. A commercial indium tin oxide (ITO) glass was used as conductive substrate, upon which a drop of the dispersion was deposited and allowed to dry [20]. EBSD data have been obtained at 20 keV, and analyzed with the CHANNEL 5 Oxford Instruments software package [27]. Transmission electron microscopy studies were performed using a FEI Titan G2 60–300 microscope operated at 300 kV. Cross-sectional TEM samples were prepared by cutting slices of the films to form a sandwich, grinding to a thickness of 50 μm and subsequent thinning to electron transparency with argon ion milling using a Gatan PIPS machine operated at 5 kV with a 10° incidence angle. Lattice spacing

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