STRUCTURAL STUDY OF TITANIUM DIOXIDE (TiO_2) NANOPOWDER PREPARED BY SOL-GEL UNDER HYPERCRITICAL DRYING

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Abstract

Nano-sized TiO_2 powders have been prepared by the sol–gel method under hypercritical conditions by hydrolyzing titanium tetra-isopropoxide. The polycrystalline structure and morphology of the powder have been characterized by X-ray diffraction (XRD), Fourier Transform InfraRed spectroscopy, scanning electron microscopy (SEM), and transmission electron microscopy (TEM). The XRD spectrum shows the anatase phase of the prepared TiO_2 powder. The energy dispersive analysis (EDS) and FT-IR confirmed the formation of TiO_2. TEM and SEM micrographs showed that the TiO_2 grains are micrometric and have irregular shapes. These grains are formed by agglomeration of TiO_2 nanocrystallites with an average size of 10 nm.

1. Introduction

In recent years, the use of titanium dioxide as photocatalyst in the air and water purification is widespread due to its considerable benefits: it is stable, inexpensive, nontoxic, more efficient, and it promotes ambient temperature oxidation of the major classes of indoor air pollutants [1]. Among the different crystalline phases of TiO_2 (anatase, rutile, and brookite), the anatase one exhibits the better photocatalytic activity but the rutile phase is the more stable and widely used for pigments and coatings. In most cases, the simultaneous presence of two phases gives better catalytic activities [2]. The synthesized of TiO_2 powder can be composed of a single phase [3] or a combination of two phases (anatase and rutile) [4]. The titanium dioxide nanocrystalline powder was synthesized by several procedures: precipitation [5], microemulsion [6], chemical vapor deposition [7], sol-gel [8] and organometallic synthesis [9]. The hydrolysis of alkoxides is often used to produce titanium dioxide. The prepared powder is often amorphous, and annealing at high temperatures is necessary to obtain crystalline structures. For low annealing temperatures, the anatase phase is dominant and a transition to the rutile occurs at 500-600°C [10]. The sol-gel technique is widely used in recent years because it can control the size, shape, size distribution, and crystalline phase of nanocrystallites. Moreover, this synthesis method is inexpensive, and chemical reactions take place at temperatures close to ambient temperature.

In this work, TiO_2 nanocrystalline powder was prepared by the sol-gel process using titanium tetra-isopropoxide as precursor under supercritical drying conditions of ethanol.

2. Experimental procedure

Titanium dioxide powder was obtained at room temperature by mixing in adequate volume proportions the titanium tetra-isopropoxide, methanol, and acetic acid solution under magnetic stirring. The ethanol and acetic acid were used as solvent and catalyst, respectively. The as-

prepared solution was placed in an autoclave and dried under supercritical conditions of pressure (63.6 bar) and temperature (243°C) of ethanol. The autoclave was filled with ethanol, and supercritical drying was started with very slow increase in temperature above the critical temperature (Tc) of ethanol. The depressurization was started after a period of 60 min in order to allow a homogeneous temperature distribution in the samples while the temperature was controlled to avoid a decrease below Tc. After this process, a TiO_2 aerogel was obtained. The X-ray diffraction (XRD) measurements were preformed with a PanAlytical diffractometer operating at 40 kV, 30 mA, using Cu-Kα radiation (λ = 1.54 Å). The as-prepared nanopowder was also characterized using a JEOL JEM-1230 transmission electron microscope (TEM), an electron beam accelerated under a high voltage of 110 kV, and a Gatan 792 CCD camera. To examine the morphology of the nanopoweder, a JEOL JSM-840A scanning electron microscope (SEM) with a link AN10/85S energy dispersive X-ray micro-analyzer operating under an accelerating voltage of 20 kV that produces a current of 1 nA and a lifetime of 100 s was used. The samples were sprayed by a small quantity of gold (Au) in order to obtain SEM micrographs. The analysis by Fourier transformed infrared (FTIR) spectroscopy was performed using KBr pellet (1 mg of the sample mixed with 300 mg KBr) using a scanning spectrometer (150 cm^{-1}/min) type Nicollet Impact 400D.

3. Results and discussion

Morphology surface scanning was done for powder using scanning electron microscopy (SEM). Figure 1 shows the SEM micrograph of the sample. The surface of the microsphere (with a diameter of about 2 μm) indicates that the as-prepared powder consists of smaller uniform primary particles. This microsphere formation process is attributed to Van der Waals forces. In order to reduce the surface energy, the primary particles have a tendency to form agglomerates, by forming spherical agglomerates, in a minimum surface-to-volume ratio and hence minimum surface free energy can be achieved [11]. The energy dispersive analysis (EDS), which is a technique associated with the transmission electron microscopy, was used to characterize the chemical nature of the powder. It shows that most elements are atoms of titanium (Ti), oxygen (O), and gold (Au). Gold was added to the characterization by SEM.

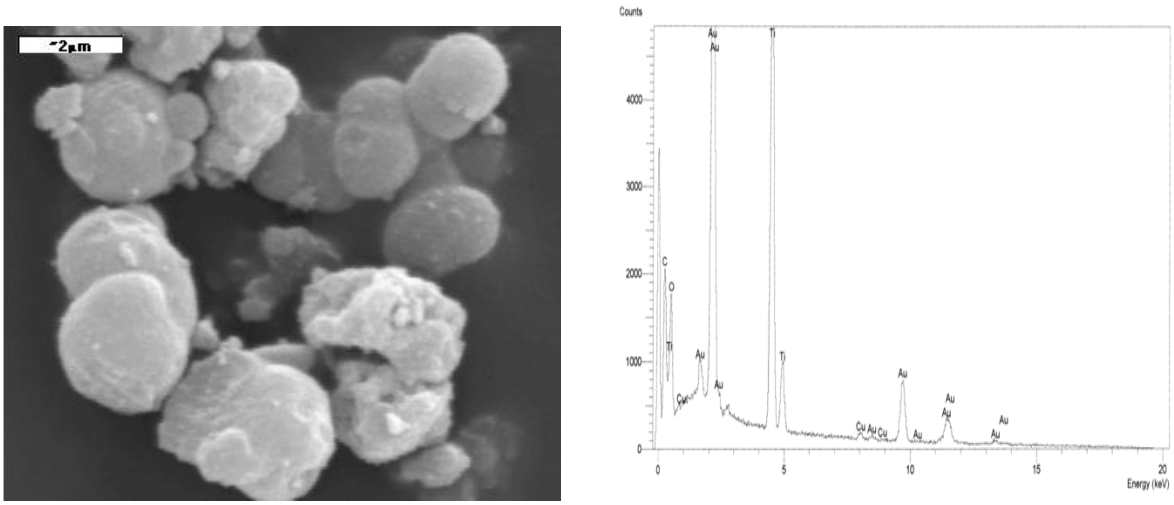

Figure 1. Typical SEM micrographs of prepared TiO_2 powder and EDS analysis.

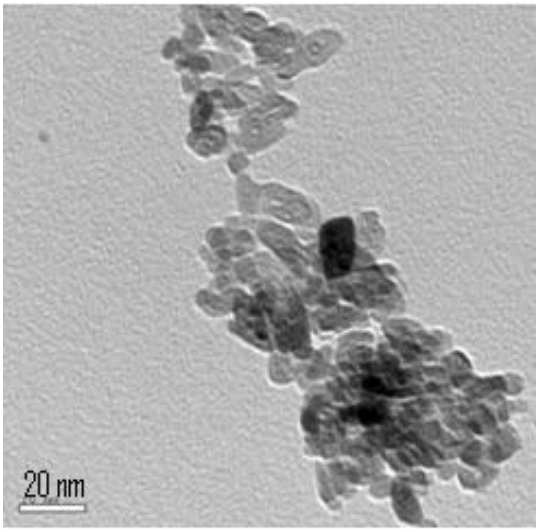

Figure 2. Typical TEM micrographs of the prepared TiO_2 powder.

The TEM image (Fig. 2) shows that the primary crystallite size is about 8-12 nm. X-ray diffraction-patterns of TiO2 powder are presented in Fig. 3. The anatase phase and polycrystalline structure of the sample are confirmed by the (101), (004), (200), (211), (220), and (215) diffraction peaks [12]. The sharp lines indicate the good crystalline quality and nanometer size of the powder crystallites. From the broadening of the line of corresponding X-ray diffraction peaks and using the Scherrer formula, the crystallite size was estimated as follows

$$D = \frac{0.89\,\lambda}{\beta cos\theta}$$

where D is the average crystallite size in nm, λ is the wavelength of the X-ray radiation (0.154 nm for copper lamp), β is the line width at half-maximum height in radians, and θ is the diffracting angle. The average crystallites size is about 10 nm which is compared with the TEM result.

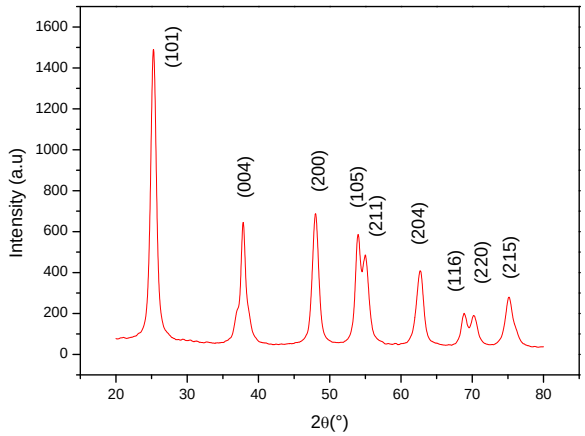

Figure 3. XRD spectrum of the prepared TiO_2 powder.

The infrared spectrum of the synthesized titanium dioxide powder in the range 4000–400 wave number is shown in Fig. 4. The large broad band at 3400 cm^{-1} can be assigned to the stretching mode and the band at 1630 cm^{-1} can be attributed to the modes.

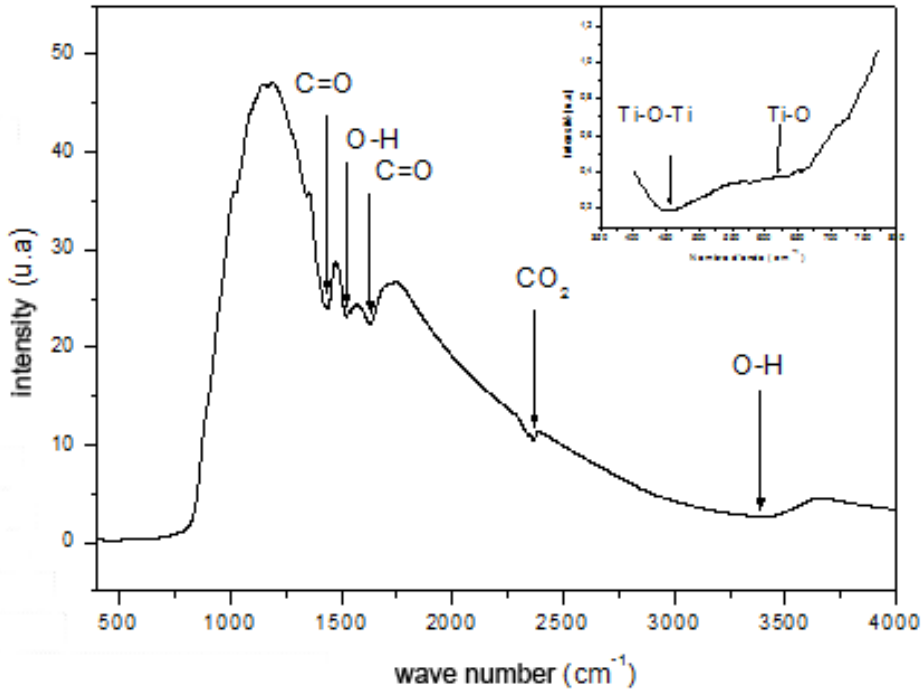

Figure 4. TiO_2 powder FT-IR spectrum. In insert: the extended spectrum between 400 and 800 cm^{-1}.

These bands are in the hydroxyl stretching region and should correspond to O–H vibration of the Ti–OH groups and H_2O molecules. CO_2 traces are also present (2360 cm^{-1}). The stretching vibrations of asymmetric and symmetric C = O are observed in 1520 and 1430 cm^{-1}, respectively. The above bands are due to the fact that the preparation of the TiO_2 powder was performed in ambient air. The vibration of the Ti-O and Ti-O-Ti bonds is observed at 650 cm^{-1} and 450 cm^{-1}, respectively (insert in Fg. 4) [13]. These bands reflect the formation of titanium dioxide TiO_2.

4. Conclusions

TiO_2 nanoparticles aerogel was synthesized by the sol–gel method using titanium (IV)-isopropoxide as a precursor. These TiO_2 particles were obtained by hydrolysis of the precursors followed by a supercritical drying in ethanol. The sample was characterized by X-ray diffraction and infrared spectroscopy. The XRD, FTIR, TEM, and SEM analysis indicated the formation of a crystalline phase (anatase) with a particle size range between 8 and 12 nm.

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