

# Microwave-Assisted Hydrothermal Method for Synthesis of Nanocrystalline Anatase TiO<sub>2</sub>

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**Abstract:** The main objective of this study is the synthesis and characterization of nanocrystalline anatase TiO<sub>2</sub> in microwave-assisted hydrothermal conditions. The synthesis was successfully performed in a microwave reaction system, Multiwave 3000, produced by Anton Paar at 2.45 GHz for a continuous power of 1000W. The structural and morphological characterization has been investigated by X-ray diffraction, DRUV-VIS spectroscopy, BET surface area analysis, SEM microscopy and EDX analysis. The material purity was confirmed by EDX elemental analysis. Results showed that the synthesized nanocrystalline TiO<sub>2</sub> contained mainly anatase phase with crystallite size of 10 nm calculated by Scherrer's relation and also confirmed by SEM images.

**Keywords:** microwave-assisted hydrothermal, TiO<sub>2</sub>, nanometer size, nanocrystalline

## 1. Introduction

The synthesis and characterization of semiconductor nanostructures (nanotubes, nanorods, and nanowires) have received considerable attention due to their exceptional properties and novel applications compared to the bulk materials. Several semiconductors have band gap energies sufficient for promoting or catalyzing a wide range of chemical reactions of environmental interest. In particular, TiO<sub>2</sub> nanostructures have been widely investigated because of their potential applications in novel photovoltaic devices, catalyst support, chemical sensors, humidity sensors, photocatalysts, solar cells, gas sensors and electrochromic devices [1-6] etc. It is well known that TiO<sub>2</sub> exhibits a relative high energy band gap (~3.2eV) and can only be excited efficiently by high energy UV irradiation that constrains the practical usage of the TiO<sub>2</sub>.

Many efforts have dedicated to the modification of TiO<sub>2</sub> nanoparticles in their morphology and phase structures through various methods, such as the hydrothermal synthesis method, sol-gel, anodization and template method [7, 8], etc. Among these means, the hydrothermal synthesis method has received particular attention owing to its technical convenience in obtaining well-structured TiO<sub>2</sub> nanostructures. Hydrothermal synthesis, in which chemical reactions can occur in aqueous or organic media under the self-produced pressure at low temperature, (usually lower than 250°C) can solve those problems encountered during sol-gel process (particles size growth, reduction of specific surface area of particles, phase transition) [9].

However, the conventional hydrothermal method usually needs high pressure and temperature, long times

and the complex procedures for obtaining of TiO<sub>2</sub> nanocrystals [10]. Hence, it is necessary to employ some alternative techniques to synthesize TiO<sub>2</sub> nanostructures. Thus, in the last years, microwave irradiation has been reported to effectively enhance the efficiency of hydrothermal method on preparation of inorganic materials [11-16]. The microwave-assisted hydrothermal method has unique advantages of uniform and rapid heating in comparison with the conventional one. In addition, this method can significantly reduce the reaction time, leading to the fast crystallization and simplification of the preparation procedure. Microwaves are also used in synthesis to improve the nanometer size fraction of particles [17]. In addition, microwaves save energy and appear today as a new technology for the development of the green chemistry, with synthesis methods involving preparation procedures based on solvent-free or reduced amount of reactant [18]. Recently, the microwave-assisted method has been used to synthesize TiO<sub>2</sub> nanostructures with different morphologies, such as nanotubes [19], nanoparticles [20] and nanorods [21].

There are several water soluble titanium precursors such as titanium isopropoxide, titanium butoxide, and titanium tetrachloride (TiCl<sub>4</sub>) used for preparation of polymorphic TiO<sub>2</sub> materials [15, 22]. TiCl<sub>4</sub> is a commercially low cost reagent for synthesis of TiO<sub>2</sub> by sol-gel, classic hydrothermal, microwave assisted hydrothermal processes.

In this study, a facile method for synthesis of nanocrystalline anatase TiO<sub>2</sub> via microwave-assisted hydrothermal method using the titanium tetrachloride as Ti precursor was developed. The physicochemical characteristics of nanocrystalline TiO<sub>2</sub> in terms of

morphology, crystallization and surface areas were characterized by scanning electron microscopy (SEM) coupled with EDX detector, X-ray diffraction (XRD), UV-VIS diffuse reflectance spectroscopy and BET surface area analyzer, respectively.

## 2. Experimental

Titanium (IV) tetrachloride ( $\text{TiCl}_4$ , 98%), oxalic acid and ethanol were purchased from ALDRICH Company.

Nanocrystalline undoped  $\text{TiO}_2$  particles were successfully prepared by microwave-assisted hydrothermal method. Therefore, 5 mL of  $\text{TiCl}_4$  was mixed with 50 ml of oxalic acid solution (5%) under continuous stirring. The obtained solutions were introduced into a Teflon autoclave with a 50% degree of fullness, for 10-30 minutes to 150-200°C, under microwave radiations (MHMW-150-10, MHMW-150-30, MHMW-200-10, MHMW-200-30). After autoclaving, the solutions were washed with distilled water and dried at 60°C for 5 hours.

The obtained materials were structural and morphological characterized by specific methods. The crystallinity of the prepared samples was measured by X-Ray diffraction (XRD) using PANalytical X'PertPRO MPD Diffractometer with Cu tube.

The light absorption properties of the materials were studied by UV-VIS diffuse reflectance spectroscopy (DRUV-VIS) using a Lambda 950 Perkin Elmer device.

A scanning electron microscopy (SEM) using Inspect S PANalytical model coupled with the energy dispersive X-ray analysis detector (EDX) was used to characterize the external surfaces of the nanocrystals, using catalyst powder supported on carbon tape.

The BET analysis was recorded with an ASAP 2020 Micromeritics system for surface area determination.

## 3. Results and Discussion

### 3.1. X-ray diffraction

Figure 1 presents the XRD patterns of undoped  $\text{TiO}_2$  synthesized by microwave-assisted hydrothermal method. It can be seen that at temperature of 150°C and autoclaving time of 10 minutes, only one crystalline phase (anatase) was obtained (Figure 1a). The specific peaks of anatase form are 2 theta: 25.3°, 37°, 37.8°, 38.6°, 48°, 54°, 55° [23]. When the autoclaving time was increased to 30 minutes rutile phase (2 theta: 27.3°, 35.9°, 41.1°, 54.1° [24]) was occurred (Figure 1b). At temperature of 200°C phase transition occurred, and at autoclaving time of 30 minutes rutile phase was predominantly (Figure 1c). This aspect is explained by the effect of annealing temperature on the anatase form, which become metastable at higher temperature and it is converted into stable rutile phase [25].

Based on the XRD patterns were calculated the particles size of the prepared materials. Crystallite size was calculated by Scherrer's formula (eq.1.) [26]

$$D = k\lambda / \beta \cos\theta \quad (1)$$

$\lambda$  is the wavelength of the X-ray radiation ( $\lambda = 0.15406$  nm),  $k$  is the Scherrer's constant ( $k=0.89$ ), and  $\beta$  is the line width at the half maximum height.

The average particle size obtained for anatase phase from XRD data for undoped  $\text{TiO}_2$  were about 10-12nm.

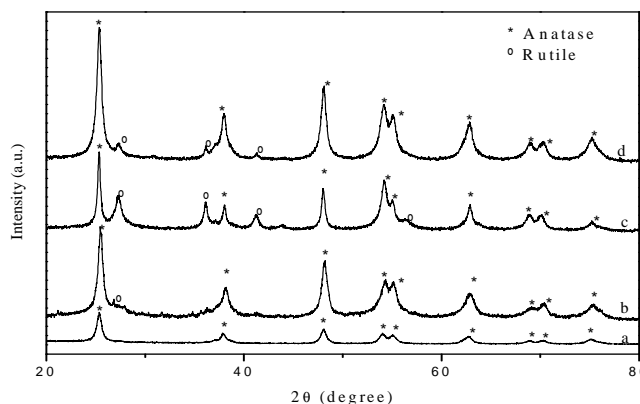


Figure 1. XRD patterns of MHMW-150-10 (a), MHMW-150-30 (b), MHMW-200-30 (c) and MHMW-200-10 (d)

### 3.2. DRUV-VIS analysis

The light absorption properties of the prepared materials crystallized in pure anatase phase were studied by DRUV-VIS performed under ambient conditions in the wavelength range of 300-600 nm. Figure 2 presents the DRUV-VIS spectra recorded for anatase form of  $\text{TiO}_2$  nanocrystals.

The obtained spectra were converted from reflexion to absorbance by Kubelka-Munk equation (eq.2) [27].

$$F(R) = \frac{(1-R)^2}{2R} \quad (2)$$

where  $R$  is reflectance.

The band-gap values are expressed by the dependence of  $(K.M-E_{bi})^2$  from  $E_{bi}$  (eq. 3)

$$E_{bi} = \frac{1240}{\lambda} (eV) \quad (3)$$

where  $\lambda$  is wavelength expressed in nanometers [28].

Spectra analysis shows that anatase form of  $\text{TiO}_2$  nanocrystals synthesized by microwave-assisted hydrothermal route adsorbs only in UV domain at the wavelength around 390 nm. Based on literature data it is known that the anatase form of undoped  $\text{TiO}_2$  has band-gap energy about 3.2eV, which means that for electrons excitation the semiconductor needs to be expose to a radiation with the wavelength smaller or equal with 385 nm, namely in UV domain [29].

### 3.3. BET surface area analysis

The surface area and pore size of the sample were measured by nitrogen isotherms. The sample was degassed for 3 h at 440°C before the measurements. The surface area for the anatase nanocrystalline  $\text{TiO}_2$  was about 50m<sup>2</sup>/g.

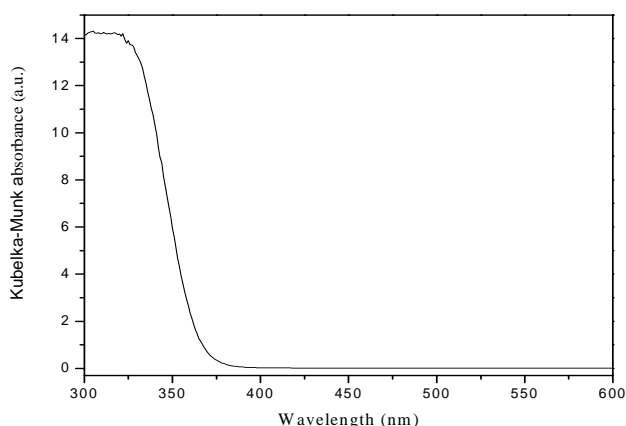


Figure 2. DRUV-VIS spectra for nanocrystalline anatase TiO<sub>2</sub> synthesized to 150°C and 10 minutes

### 3.4. SEM/EDX analysis

For the morphological and structural characterization the anatase nanocrystalline TiO<sub>2</sub> was characterized by SEM morphology and EDX analysis (Figure 3).

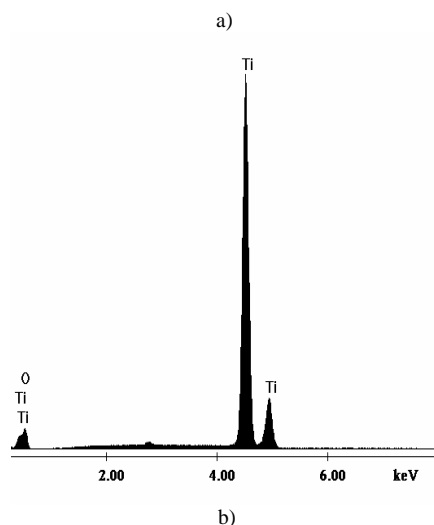
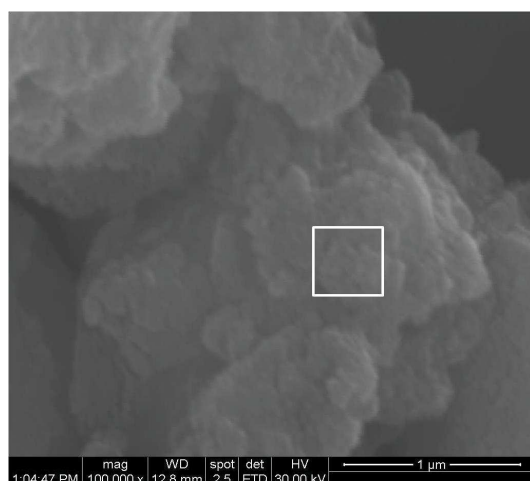


Figure 3. a) SEM morphology and b) EDX analysis for anatase nanocrystalline TiO<sub>2</sub>

SEM image evidenced the spherical form of TiO<sub>2</sub> nanocrystals, specific for anatase phase [30] highly agglomerated in asymmetric conglomerates (Figure 3a). Also the nanometer size of the particle was confirmed at 12-15nm. EDX microprobe provided a semiquantitative elemental analysis of the surface indicating the materials purity. Thus, for undoped TiO<sub>2</sub> (Figure 3b) EDX spectra evidenced the Ti and O presence.

## 4. Conclusions

Nanocrystalline anatase TiO<sub>2</sub> were successfully obtained by microwave-assisted hydrothermal method using titanium tetrachloride like Ti precursor. Based on XRD patterns the optimum annealing temperature was set up at 150°C and the autoclaving time at 10 minutes. The average particle size obtained for anatase form calculated by Scherrer's equation was in the nanometer range, 10-15 nm. SEM images presented the spherical form of TiO<sub>2</sub> nanocrystals, specific for anatase phase and also confirmed the nanometer particle size. EDX analysis confirmed the materials purity and presence of Ti and O ions.

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