

## Conference Paper

# Sol-Gel Synthesis of Nonstoichiometric Titanium Dioxide for Photo-Oxidation of Toxic Organic Substances

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## Abstract

Titanium dioxide (TiO<sub>2</sub>) was synthesized by sol-gel method at different values of pH = 3, 7, 8, 9, or 10. X-ray phase analysis has shown that in an acid rout, an anatase phase had crystallized, and in an alkaline rout an amorphous phase of TiO<sub>2</sub> was achieved. After annealing for 4 hours at 350°C, all samples were transformed into anatase phase. The particle size in the different samples varies from 7 to 50 nm depending on the pH. The diffuse reflectance spectra revealed a high value of the band gap width in the range from 2.9 to 3.4 eV and its narrowing after annealing to the range from 2.8 to 3.1 eV. The specific surface area measured by BET method was changing from 80 up to 140 m<sup>2</sup>/g.

**Keywords:** Titanium dioxide, nanostructure, photocatalysis, band gap, specific surface area.

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Published: 31 December 2020

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Selection and Peer-review under the responsibility of the TECHNOGEN-2019 Conference Committee.

## 1. Introduction

Nowadays, nanoscale modifications of titanium dioxide (nano-TiO<sub>2</sub>) are of great interest due to their prospective for use as functional media of renewable energy sources, inorganic sorbents, resistive memory elements, application in nanobiomedicine as part of complex hybrid designs for targeted delivery medicines, in photocatalysis, etc. [1–9]. The functionality of nano-TiO<sub>2</sub> in a certain field of their application is determined by the properties of the substance and there are some problems in synthesizing a material with specified characteristics. To synthesize titanium dioxide nanoparticles a large number of different methods are used, such as solvothermal, hydrothermal, anodic oxidation, chemical vapor deposition, electrodeposition, sonochemical and microwave method [4, 6, 7, 10, 11]. These methods require particular equipment and special conditions for synthesis, which complicates the process of synthesizing titanium dioxide and makes it costly. Sol-gel method is simple in application and low-cost, it allows to synthesize nanodispersed powders with the ability to regulate the structural properties of the

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material when choosing the appropriate conditions for the synthesis [12–14]. However, despite the active study of titanium dioxide synthesized by sol-gel method, there is currently no clear and comprehensive understanding of the synthesis parameters effect on the formation of  $\text{TiO}_2$  nanoparticles in various modifications (amorphous, anatase, rutile and brookite). One parameter that significantly affects the final product is the starting pH value of the solution. In this regard, the aim of the work was to study the effect of the acid-base state of the solution on the obtained structure of titanium dioxide. For this,  $\text{TiO}_2$  was synthesized by sol-gel method at various pH values (3, 7, 8, 9 and 10) and followed by annealing, X-ray phase analysis (XRD) of the product was performed, its crystal modification is determined, spectra of diffuse reflection (DRS) were measured, the values of the particle size and band gap ( $E_g$ ) were calculated before and after annealing of samples.

## 2. Experimental Part

Five samples of nanosized titanium dioxide ( $\text{TiO}_2$ ) were synthesized by sol-gel method at different pH of the initial solution – 3, 7, 8, 9 and 10. Titanium tetrabutoxide (tetrabutoxytitanium)  $\text{Ti}(\text{C}_4\text{H}_9\text{O})_4$  (analytical grade A.C.S.), ethanol  $\text{C}_2\text{H}_5\text{OH}$  (95%) and distilled water  $\text{H}_2\text{O}$  were used as initial reagents in a volume ratio of 1:1:4. The acid-base state of the solution was varied by the addition of hydrochloric acid HCl (analytical grade A.C.S.) to obtain an acid medium and ammonium hydroxide  $\text{NH}_4\text{OH}$  (aqueous solution 10%) to produce an alkaline medium. Synthesis of titanium dioxide was carried out according to the following scheme. Tetrabutoxytitanium was mixed with ethanol until a homogeneous state in a mixing device PE-6300 M for 10 minutes, and after that distilled water was added and stirred again in device for 10 minutes. Then, HCl or  $\text{NH}_4\text{OH}$  was added in an amount, which was necessary to achieve the desired pH, followed by stirring for 60 minutes. The parameters of the mixing device at all stages were the same: substrate temperature of 60 °C, power of 80 W, rotation speed of 26 rpm. The resulting gel was dried in SNOL oven for 60 min at 80 °C. Synthesized  $\text{TiO}_2$  powders were subsequently annealed in a SNOL muffle furnace for 4 hours at 350 °C.

The titanium dioxide powders synthesized by the sol-gel method was investigated by XRD using  $\text{CuK}\alpha_{1,2}$  radiation on a Shimadzu XRD-7000 diffractometer with the Bragg–Brentano recording geometry. XRD patterns were measured using the step-scan mode at  $\Delta(2\theta) = 0.02^\circ$  in the  $2\theta$  angular range from 10 to 100° with 10 sec exposure time at

each point. The diameter of the coherent scattering regions (CSR) which is closed to the size of the titanium dioxide nanoparticles were calculated from the Scherrer formula

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

where  $K$  is particle shape factor;  $\lambda$  is X-ray wavelength (154 pm);  $\beta$ =FWHM is full width at half maximum;  $\theta$  – diffraction maximum position. Relative deviation of calculations  $D$  was 10 %.

Diffuse reflectance spectra (DRS) of the samples were recorded on a FS-5 (Edinburgh Instruments) UV-VIS spectrophotometer. The values of the band gap energies were determined from diffuse reflection spectra using Kubelka-Munk function:  $(h\nu F(R))^2$ , where  $R$  – reflectance,  $h$  – Planck constant,  $\nu$  – frequency and  $F(R) = \frac{(1-R)^2}{2R}$ . Relative deviation of calculations of  $E_g$  was 10%. Specific surface area was determined by the Brunauer-Emmett-Teller method (BET) using a Gemini VII 2390 analyzer. Preliminary degassing of samples was carried out for 2 hours at 200 °C.

### 3. Results and Discussion

The XRD analysis of the synthesized TiO<sub>2</sub> powders showed that at pH = 3, titanium dioxide has a crystalline anatase phase. On XRD patterns of samples obtained at higher pH, from 7 to 10, small broadening and complete absence of diffraction peaks are observed near the angles  $2\theta$  – 30°, 45°, and 65°, which indicates that synthesized powders have an amorphous structure. Probably, using the acidic medium of the initial sol, crystallization process is active even at low temperatures about 80 °C without annealing. Also, X-ray phase analysis showed that annealing led to a phase transition from the amorphous phase to anatase. The choice of the annealing temperature of 350 °C is due to the desire to get an anatase structure without the formation of rutile modification, which was received in earlier experiments at an annealing temperature of 450 °C. According to XRD data, there is no influence of pH from 7 to 10. Indeed the XRD patterns have a similar appearance. Determination of the specific surface area measured by BET method showed that the minimum area is observed for samples obtained at pH = 10, and maximum at pH = 7. All powders differ in color, in width of the band gap ( $E_g$ ), in nanoparticle diameter ( $D$ ) and in specific surface area value (see Table 1).

The calculation of the CSR of nanostructured titanium dioxide in the anatase phase (after annealing) indicates a change in the particle size at different pH values (Table 1). The particle size increases linearly from 7 to 50 nm as the pH increases from 3 to 9. At a pH value of 10, the particle size reaches 25 nm, this value coincides with the

TABLE 1: Physical characteristics of titanium dioxide powders synthesized by the sol-gel method at various pH values.

$pH, \pm 0.1$	$D, \pm 2 \text{ nm}$	$E_g \text{ before annealing, } \pm 0.2 \text{ eV}$	$E_g \text{ after annealing, } \pm 0.2 \text{ eV}$	$S_{\text{eff}}, \pm 1 \text{ m}^2/\text{g}$
3	7	2.9	2.8	100
7	10	3.2	3.1	140
8	25	3.4	3.1	90
9	50	3.2	2.8	90
10	25	3.4	3.0	80

particle size at pH 8 (25 nm). It should be noted that the powder color at a substantially equal value of the same size – a light beige, and at maximum particle size – most dark (yellow). In the diffuse reflection spectra, the region of increase in the reflection intensity shifts toward the UV range with increasing pH. Starting increasing reflectance is near 350 nm, it coincides with the data DRS nanosized titanium dioxide obtained in other ways: solvothermal, sonochemical and polyol methods [11], but the reflection intensity of the samples studied in this work is lower, which indicates a greater absorption, and hence a greater number of atomic-vacancy defects in the structure. In the visible region of the spectrum (about 400 nm), in all annealed samples obtained at  $pH > 7$ , a diffuse reflection collapse is observed. This effect is also observed in other studies on the effect of the solution pH on the titanium dioxide structure [14]. This is probably due to the nonstoichiometry of titanium dioxide in the anatase phase and the formation of oxygen vacancies in the crystal structure. Atomic defects in the crystal structure form energy levels in the band gap, resulting in visible light absorption occurs at a wavelength between 400 and 430 nm [6, 7]. The performed DRS analysis of all samples before and after annealing with using Kubelka-Munk function allowed determining the band gap width of synthesized titanium dioxide (see Table 1). All samples with an amorphous structure have a wide band gap (from 2.9 to 3.4 eV), but upon transition to the anatase phase these values decrease by 0.1 – 0.4 eV. The smallest value of  $E_g$  is observed in the sample taken at  $pH = 3$ , and at higher pH values, the width of the band gap increases. These data do not correspond to an earlier work, where with an increase of pH from 2.6 to 10.6, the band gap decreases from 3.6 to 3.0 eV [12]. Perhaps this is due to the difference in using of specific chemical reagents for sol-gel synthesis and the different final particle sizes values of the synthesized titanium dioxide.

## 4. Conclusion

In this paper, the influence of the initial solution pH on nanosize of the titanium dioxide synthesized by sol-gel methods was studied. XRD data showed the formation of the

anatase crystal structure in an acidic medium even without annealing and amorphous structure in neutral and alkaline media. The crystallization process acceleration of titanium dioxide in the synthesis with pH = 3 was revealed. Annealing at 350 °C for 4 hours allows a phase transition from an amorphous modification to anatase without the formation of rutile. The calculation of the TiO<sub>2</sub> particle size was carried out from XRD patterns using Scherrer formula, they are in the range between 7 and 50 nm. The crystal structure of the synthesized samples at pH = 7 - 10 according to XRD data has no distinct differences, but structure has a different nonstoichiometry according to DRS analysis. The  $E_g$  value for all samples was calculated before and after annealing upon conversion of DRS into Kubelka-Munk function. A wide band gap was found in all samples amorphous modification (2.9 to 3.4 eV), and its reduction after annealing of titanium dioxide at the transition into the anatase phase (2.8 to 3.1 eV). The detected rather high specific surface area value (80-140 m<sup>2</sup>/g) of nanosized titanium dioxide can lead to its high photocatalytic activity.

Thus, it was shown that the sol-gel method allows receiving nanoscale titanium dioxide with different size of particles by changing of pH solution. The proposed method for TiO<sub>2</sub> synthesis is simple, reliable, low-cost and allows controlling the parameters of the final product by choosing the optimal process conditions. Therefore, in this work, we have suggested and synthesized a catalyst, which can to neutralize toxic organic substances in the UV, as well as in the visible regions of the optical spectrum.

## Acknowledgements

The work was carried out according to the state assignment for IMET UB RAS and ISSC UB RAS.

I.A. Weinstein thanks Minobrnauki initiative research project № FEUZ-2020-0059 for financial support.

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