

# Preparation of TiO<sub>2</sub> nanoparticles by *Sol-Gel* route

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**ABSTRACT.** Nanosized titanium oxide (TiO<sub>2</sub>) powders were prepared by emulsification-gelation technology, hydrolysis and reflux process. Starting precursor (Tetraisopropylorthotitanate Ti(OC<sub>3</sub>H<sub>7</sub>)<sub>4</sub>) was modified by 1,4 cyclohexane diol (C<sub>6</sub>H<sub>14</sub>O<sub>2</sub>), hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) and Triethanol amine (C<sub>6</sub>H<sub>15</sub>NO<sub>3</sub>). Titanium tetrachloride was also used as precursor. The effect of methanol on ethanol solvent was also investigated. The powders were analyzed by X-ray diffraction (XRD) and BET technique. Scanning electron microscopy observation was used for agglomerate observations. The photoactivity of the products obtained was taken as efficiency of Benzamide photodegradations.

## 1. INTRODUCTION

In recent years the photocatalytic decomposition of pollutant in water has received much attention [1–4]. This process is of particular interest due to its ability to use solar energy. When TiO<sub>2</sub> was irradiated with wavelength greater than 390 nm, electron-hole pairs were generated. One of the major limits of using TiO<sub>2</sub> as photocatalyst is their relatively low value of overall quantum efficiencies, combined with the necessity of using near ultraviolet radiation. Some success in enhancing the photocatalytic activities is obtained by the preparation of TiO<sub>2</sub> nanoparticles. The effect of crystallite size and quantum size effect is observed in gaseous photocatalytic hydrogenation of acetylene with H<sub>2</sub>O [5]. However, there are few studies on photocatalytic activity of nanoparticle TiO<sub>2</sub> crystallites in aqueous suspension systems.

Several methods of TiO<sub>2</sub> preparation have been reported in literature based on the hydrolysis of acidic solutions of Ti (IV) salts. Also, oxidations of TiCl<sub>4</sub> on gaseous phase [6–8] and hydrolysis of titanium alkoxides [9, 10] have been used to generate finely divided with a high purity TiO<sub>2</sub> powders.

In the present work, we have prepared different TiO<sub>2</sub> nanoparticles using several precursors and different procedure preparations. The photocatalytic activity of the materials obtained was used for Benzamide photodecompositions in aqueous solution. Benzamide is not adsorbed on TiO<sub>2</sub> surface and its photodegradation mechanism is well known [11]. Moreover, it can be considered as a model pollutant.

## 2. EXPERIMENTAL

**2.1. Reagents.** The following commercial reagents were used without any further purifications: Tetraisopropylorthotitanate Ti(OC<sub>3</sub>H<sub>7</sub>)<sub>4</sub> (TIPT), purity 99%; Titanium tetrachloride (TiCl<sub>4</sub>), purity 99.9%; Ethanol (EtOH) absolute grade, purity 99.9%; Methanol (MeOH)

absolute grade, purity 99.9%; n-Hexane CH<sub>3</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub>, purity 99%; Hydroxypropyl cellulose P.M. 100.000 (HPC); 1,4 CycloHexane diol C<sub>6</sub>H<sub>14</sub>O<sub>2</sub> (CHD), purity 99%; Triethanol amine C<sub>6</sub>H<sub>15</sub>NO<sub>3</sub> (TEA), purity 99%; Agar-Agar pure. TiO<sub>2</sub>-P25, purity 99.8% (degussa Corporation).

**2.2. Preparation of TiO<sub>2</sub> nanoparticles.** Method 1: TIPT and CHD were dissolved in 300 ml of absolute EtOH with the molar ratio (1 : 1). The reaction mixture was stirred at 80 °C for 3 h. After cooling, a controlled amount of water was added drop-wise to the solution.

Method 2: TIPT was slowly added to a basic solution (pH~9) of hydrogen peroxide H<sub>2</sub>O<sub>2</sub> (200 ml, 3.6 M) under stirring at 5 °C. The yellow gel observed indicates the formation of peroxide complex of Titanium.

Method 3: This is a variation of method 2, where the peroxide complex of Ti is substituted by a complex obtained by dissolution of TIPT in TEA (TEA/TIPT molar ratio: 0.5)

The initial pH of solutions obtained from the method 1 to 3 were adjusted to 6 by NH<sub>4</sub>OH or HNO<sub>3</sub>, and then dispersed in 100 ml of hexane with the presence of surfactant (Agar-Agar) 10<sup>-2</sup> g/ml as emulsifying agents. After gelation, stirring was continued for 1 h. The gel was filtered and washed subsequently by water (500 ml) and EtOH (200 ml), dried at room temperature for 12 h.

Method 4: In order to get nanostructured TiO<sub>2</sub>, the TIPT solution is dissolved in a mixture of MeOH and EtOH with molar ratio (1 : 1 : 10) and refluxed at 60 °C for 6 h. Water is added drop wise into the hot solution (60 °C). The precipitate is isolated by filtration, washed with hot water and organic solvents to remove the adsorbed impurities, and heated at 130 °C for 12 h.

Method 5: TiCl<sub>4</sub> was added dropwise and under stirring to 500 ml of water at about 0 °C. The colloidal TiO<sub>2</sub> solution was dialyzed until the pH lay between 2 and 3. The solvent was removed by rotary evaporation.

Method 6: The present method of synthesis is an adaptation of the method used by K. D. Kim and H. T. Kim [12] for the preparation of TiO<sub>2</sub> nanosized using a two-stage mixed method. The starting solution containing water 70% and alcohol 30% (MeOH and EtOH in the ratio 1 : 10) was added dropwise to a solution containing: TIPT + HPC + alcohol. Thereafter, the mixture resulting at the first stage was agitated for 60 min under Ar atmosphere. When the first stage reaction (semi bath) was finished, the bath reaction (the second stage) was started. Two solutions containing respectively (water + alcohol) and (TIPT, HPC, alcohol) were added to the solution obtained from the first stage. The resulting mixture was vigorously stirred during 60 min. The powders were isolated by repeated centrifugation and dried at 70 °C for 12 h.

The obtained products were treated at 550 °C for 2 or 10 hours in air.

**2.3. Catalyst characterization.** Powder X-ray diffraction (XRD) was used for crystal phase identification and estimation of the anatase: rutile ratio and the crystallite size of each phase present. The XRD intensities of anatase (101) peak and rutile (110) were analyzed. The percentage of rutile in the samples can be estimated from the respective integrated XRD [9]. The crystallite size can be determined from the broadening of corresponding X-ray spectral peaks by Scherrer formula. XRD patterns were obtained at room temperature with a diffractometer using Cu K<sub>α</sub> radiations. Scanning electron microscopy (SEM) observations were performed using a HITACHI S2500. The specific surface area of TiO<sub>2</sub> resulting from different methods of preparations was determined by using nitrogen adsorptions (BET method).

**2.4. Photoactivity.** The benzamide was used as supplied. In each run, 500 mg of prepared TiO<sub>2</sub> powder was added into a 1000 ml Pyrex vessel containing 500 ml of 10 mg of benzamide solution ([Benzamide] = 20 mg/l). The mixture was sonicated before irradiation for 5 min. The stirred suspension was irradiated in solar box ATLAS Suntest CPS+ simulating natural radiation. The light source was a vapour Xenon lamp (300 nm < λ < 800 nm). The photoactivity of each TiO<sub>2</sub> was evaluated by the rate of benzamide disappearance. For this purpose, benzamide concentrations at different irradiation times were followed by HPLC equipped with a C18 column after filtration (Watmann filter, 0.45 μm). The pH of the solution was not controlled. The vessel was opened to air and samples were taken out in regular time intervals for the determination of benzamide concentration.

### 3. RESULTS AND DISCUSSION

From the product of the methods 1 to 3, transparent and acceptable rigid gels were obtained in a short time

(~ 1 h) by adjusting the pH of the solution to 6. Miukami *et al.* [13] observed the reaction occurring in method 1, several trans enolizations can be envisaged between alkoxides and cyclohexane diol resulting in the formation of different binuclear complexes. However, it is known that Titanium alkoxides can react with cyclic diols giving rise to liquid chelate monomers [14]. In our experimental condition, gel formation has not been seen, till the gellation stages.

As regards the reactions involved in the formation of the sol by method 2, Ti (IV) in the presence of hydrogen peroxide gives an intense yellow color depending on concentration solutions, characteristic of peroxo-complexes, such as peroxytitanato ion [Ti(OH)<sub>3</sub>O<sub>2</sub>]<sup>-</sup>, also named peroxytitanic acid. The mechanism formation of peroxytitanic is very complex and not completely known. However, F. A. Cotton *et al.* [15] suggested, when titanium metal was used as starting materials at pH ~ 11 the following reaction:



Hydrogen peroxide must be in excess to stabilize the solution of peroxytitanic. When H<sub>2</sub>O<sub>2</sub> was substituted to TEA, a stable species was generated with Ti Alcoxide [16].

On method 4 we have used a mixture solvent containing methanol and ethanol to investigate the effect of the presence of methanol on physico-chemical properties of TiO<sub>2</sub>.

TiO<sub>2</sub> prepared by hydrolysis of TiCl<sub>4</sub> in aqueous solution has been the subject of extensive works. The size and morphology of grain was found to be depending on a few parameters such as hydrolyse temperatures, [H<sub>2</sub>O]/[Ti<sup>4+</sup>] ratio and thermal treatment conditions [17]. When TiCl<sub>4</sub> hydrolyses, TiO<sub>2</sub> particles were generated as well as H<sup>+</sup> and Cl<sup>-</sup> ions, the process can be described by the following reaction:



When TiCl<sub>4</sub> was added to aqueous solutions, the heat of exothermic reaction was observed. The precipitations of TiO<sub>2</sub> occur only when pH of solutions was higher than 2.

Method 6 depends on a few parameters such as reactants concentration (TIPT: H<sub>2</sub>O: MeOH), dispersion (volume of EtOH), quantity of HPC used, temperature of bath in both stages. All these parameters have not been optimized. HPC was used as a dispersant to prevent agglomeration during particle growth.

**3.1. Characterization of prepared TiO<sub>2</sub> materials.** A thermal treatment is necessary to improve the crystallinity of amorphous compounds. When TiO<sub>2</sub> powders are calcinated at higher temperature, crystal structure transformations may occur. The amorphous-anatase and anatase-rutile transitions depend strongly

on the method preparations, the nature of the precursor and calcination conditions. Generally, the complete transformations of amorphous to anatase has been found to be completed between 350 °C and 450 °C, the anatase-rutile transformation has been reported to occur in different temperature ranges from 600 °C to 1100 °C [18].

Typically, the XRD patterns for different products calcinated at 550 °C for 10h were found to be more crystallizes than the same products calcinated at 550 °C for 2h. The products calcinated at 550 °C for 10h indicate different stages of crystallizations (Figure 1), depending on the nature of the precursor and the procedure of preparation. Furthermore, the samples prepared from the organic precursors presented more ability to form a high crystallinity than the samples generated from mineral precursors such as titanium tetrachloride and titanium peroxide in our experimental conditions. The peaks of the samples prepared by methods 4 and 6 were weak in comparison with others calcinated in the same conditions. This indicates a high

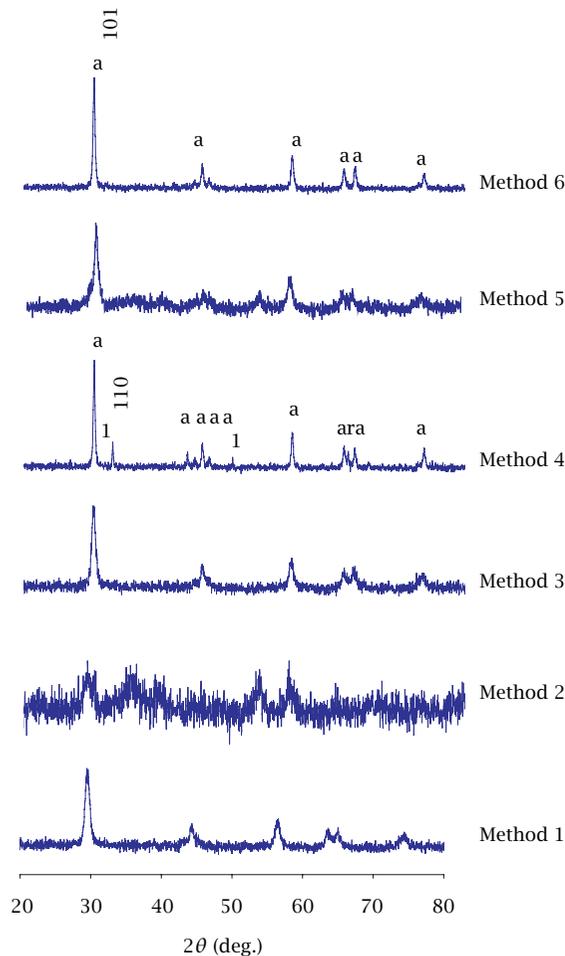


Figure 1. XRD patterns of TiO<sub>2</sub> photocatalysts treated at 550 °C for 10h.

level of crystallizations. XRD analysis of the samples prepared by method 4 (Figure 1) showed the existence of anatase and rutile with the ratio 23% by weight of rutile close to that observed for TiO<sub>2</sub> P25.

The crystallite size was estimated by Scherrer formula. This method is generally accepted to estimate the mean particle size. The result is summarized in Table 1. In all cases, the particle size doesn't exceed 40 nm and the smaller crystallite was obtained with method 1 (size varied between 7 and 10 nm). A higher specific surface was also obtained by this method (44.5 m<sup>2</sup>g<sup>-1</sup>) compared with other methods that can't exceed ~ 20 m<sup>2</sup>g<sup>-1</sup>.

Scanning Electron Microscopy (SEM) observation showed high homogeneity of the samples prepared by method 1. The aggregate formed by the emulsifant-gelation technology has an average size in the range of 0.4 μm (Figure 2). The samples prepared by using reflux process (method 4) revealed two types of aggregates with a different average size. In the first type, the aggregate has a spherical shape with an average diameter of 1 μm and for the second one, 0.2 μm diameters can be observed.

**3.2. Photocatalytic activity.** The photoactivity of TiO<sub>2</sub> was investigated using benzamide (BZ) as the representative aromatic pollutant. In our experimental condition a direct photolysis of BZ has not been observed, and the photocatalytic degradation of BZ can be attributed to the hydroxyle radicals OH<sup>•</sup>. These radicals are formed by the reaction between adsorbed OH<sup>-</sup> at the TiO<sub>2</sub> surface and the holes "h<sup>+</sup>" on the valence band. Adsorptions of BZ at the surface of each TiO<sub>2</sub> did not occur in all cases.

Maillard *et al.* [11] have identified several intermediates when BZ is photodegraded on aqueous solutions. In the first stage, monohydroxylation of the aromatic ring occurs in the three positions *ortho*, *meta*, and *para* to the amide group. Furthermore, *para*-benzoquinone and *ortho*-hydroquinone were identified and attributed to the second stage degradation mechanisms.

In general, the photocatalytic activity of the samples treated at 550 °C for 10h was found to be higher than the samples treated for 2h. This fact could be associated to the more crystalline structure observed for the samples calcinated for 10h though this long treatment induces the decrease of the specific area.

In our case, the more influencing parameter is the level of crystallinity which can be concluded from the results of photocatalytic activity. The crystallinity and surface area are two parameters involving on different ways.

Figure 3 shows the decreasing concentration of BZ versus irradiation time for the samples prepared by method 4. The effect of heat treatment can be seen, confirming the high photoactivity concluded for the samples treated at 550 °C for 10h. TiO<sub>2</sub> calcinated for 2h

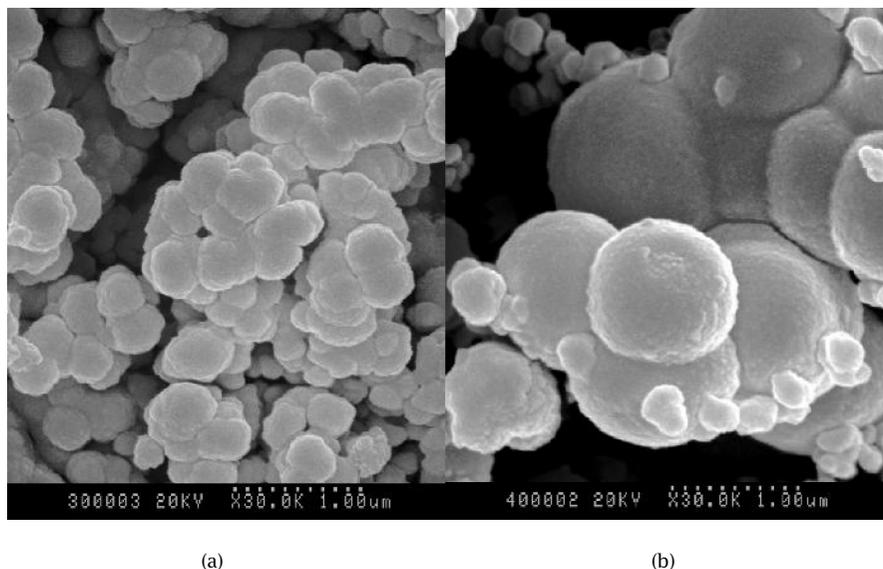


Figure 2. SEM micrograph of  $\text{TiO}_2$  agglomerate after calcinations at  $550^\circ\text{C}$  for 10 h resulting from: (a) Method 1 (b) Method 4.

Table 1. Physical properties of obtained  $\text{TiO}_2$ .

Thermal treatment duration		Method 1	Method 2	Method 3	Method 4	Method 5	Method 6
2 h	L (nm)	7.92	19.81	13.21	19.87	—	23.23
	S ( $\text{m}^2\text{g}^{-1}$ )	44.5	—	23.1	17.2	14.9	6.7
10 h	L (nm)	10.02	20.24	13.21	19.81	17.23	39.65
	S ( $\text{m}^2\text{g}^{-1}$ )	32.07	—	19.50	14.00	15.4	6.8

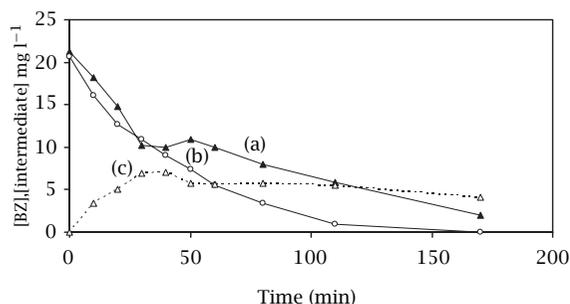


Figure 3. Benzamide degradations using  $\text{TiO}_2$  resulting from method 4 preparations: (a) after 2 h at  $550^\circ\text{C}$ , (b) after 10 h at  $550^\circ\text{C}$  (c) intermediate concentration procedure (a).

present a non-conventional degradation curve. At the beginning, the concentration of benzamide decreased regularly with time and then stopped when  $\sim 50\%$  of BZ was removed (after 30 min of irradiation). After 30 more minutes, the degradation restarted. These phenomena can be attributed to the preferential adsorption of intermediate products at the surface of semi-conductors which can react preferentially to benzamide. In fact,

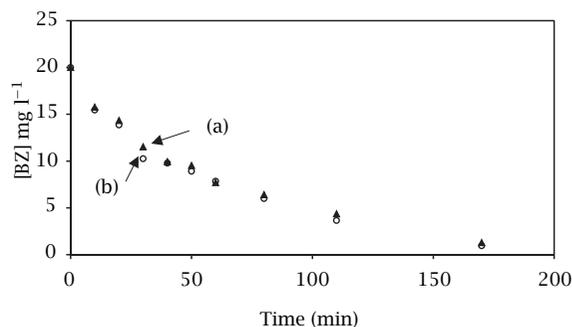


Figure 4. Benzamide degradations using  $\text{TiO}_2$  resulting from method 6 preparations: (a) after 2 h at  $550^\circ\text{C}$ , (b) after 10 h at  $550^\circ\text{C}$ .

the maximum concentrations of intermediate were observed when the degradation rates become close to zero (Figure 3). This particularity can be used for selective degradation of compounds such as 4-hydroxy benzamide or others in the presence of BZ using this  $\text{TiO}_2$ .

The products resulting from method 6 preparations were found to be time treatment independent (*i.e.* the same photoactivity was observed after being treated for 2 or 10 h at  $550^\circ\text{C}$ , Figure 4). This due to the fact that we

have obtained in both cases a high level of crystallinity and the same specific surface ( $\sim 6.8 \text{ m}^2 \text{ g}^{-1}$ ).

The results of photoactivity of different TiO<sub>2</sub> calcinated at 550 °C for 10 h can be observed in Figure 5. The products resulting from methods 2, 3 and 5 showed a low photoactivity. Indeed, this compartment is attributed to the poor crystallinity observed by X-ray analysis. The amorphous characters of compounds induces high concentrations of defects. Each one acts as a recombination center when electron and hole were generated under illuminations [19].

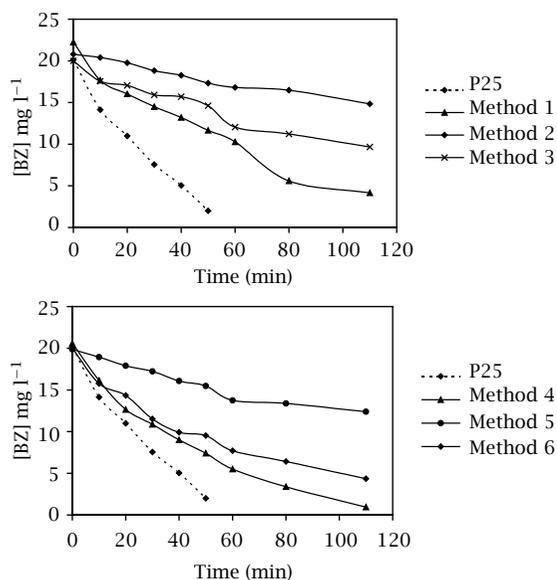


Figure 5. Photocatalytic degradation of BZ using TiO<sub>2</sub> generated from different methods and calcinated at 550 °C during 10 h.

The same photoactivity was obtained when TiO<sub>2</sub> from methods 6 and 1 were used though both compounds have different physical properties. The very low specific surface ( $6.8 \text{ m}^2 \text{ g}^{-1}$ ) is compensated by a high level of crystallinity for method 6 products. In addition, the interesting surface area obtained from method 1 ( $32.7 \text{ m}^2 \text{ g}^{-1}$ ) confer sufficiently active surface to compensate the moderate crystallinity. The very small crystallite size ( $\sim 10 \text{ nm}$ ) implies a high number of particles, each particle acts like nanophotochemical radical generators.

The effect of rutile–anatase distribution on photocatalytic activity of TiO<sub>2</sub> can be observed by using the product resulting from method 4. In fact, the best result of photoactivity was obtained close to that observed for TiO<sub>2</sub> P25. The higher crystallinity combined with good surface state improve the photocatalytic performance. However, the surface area obtained from this new method of preparations is low in comparison to TiO<sub>2</sub>-P25 ( $50 \text{ m}^2 \text{ g}^{-1}$ ).

It should be taken into account that this new method of preparation combining two alcohols has not been optimized. Nevertheless, the optimization of method 4 in progress in our laboratory shows the high influences of precursor, methanol and water ratios. Temperature and time of the refluxed process are under investigation.

#### 4. CONCLUSION

The research work presented in this paper leads us to draw the following conclusions. TiO<sub>2</sub> nanoparticles were successfully prepared with a crystallite size between 8 nm and 40 nm. The effect of modified precursor was observed from the product prepared by emulsification-gelation technology. In fact, by using 1,4 cyclohexane diol as a modified precursor, the product calcinated for 10 h at 550 °C showed a single anatase phase with  $\sim 10 \text{ nm}$  crystallite size, also the surface area was found to be close to TiO<sub>2</sub>-P25. High homogeneity of aggregate was obtained from SEM observation with an average size of  $0.4 \mu\text{m}$ . For the same technique preparations, using hydrogen peroxide and triethanolamine as modified precursor, TiO<sub>2</sub> on nanoparticles were obtained. However, a low level of crystallinity was obtained from the results of XRD analysis. Regarding the photocatalytic benzamide degradations we have a best result, when 1,4 cyclohexane diol was used.

For other methods of preparation, the best photoactivity was obtained from the product prepared by reflux process and heated at 550 °C for 10 h. XRD analysis of this sample showed the presence of anatase and rutile phases close to that observed for TiO<sub>2</sub>-P25 (23% of rutile). The crystallite size of this product was found to be less than TiO<sub>2</sub>-P25. SEM showed two type of aggregate. In the first type, the aggregate has spherical shape with average diameter of  $1 \mu\text{m}$  and for the second one,  $0.2 \mu\text{m}$  diameter can be observed.

From the physico-chemical properties of prepared materials and their efficiency of benzamide photodegradation, we can conclude that the level of crystallinity is a deciding factor for benzamide degradation and there is no evidence of relations between photocatalytic performance and surface area.

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