

SYNTHESIS, PHOTOCATALYTIC AND ANTIBACTERIAL PROPERTIES OF NANOSIZED ZnTiO₃ POWDERS OBTAINED BY DIFFERENT SOL-GEL METHODS

A. STOYANOVA*, H. HITKOVA, A. BACHVAROVA-NEDELICHEVA^a, R. IORDANOVA^a, N. IVANOVA, M. SREDKOVA

Medical University, 5800 Pleven, Bulgaria.

^aInstitute of General and Inorganic Chemistry, BAS, "Acad. G. Bonchev" str., bl. 11, Sofia, 1113, Bulgaria

Zinc titanate (ZnTiO₃) is an attractive material due to its various applications as paint pigment, microwave dielectrics, catalysts, etc. In this work nanosized ZnTiO₃ powders were synthesized by means of aqueous and nonaqueous sol-gel methods. For the synthesis of zinc titanate by aqueous route zinc acetate and titanium ethoxide were used as starting materials. The synthesis of nanocrystalline ZnTiO₃ by a nonaqueous route was based on the reaction between TiCl₄, ZnCl₂ and benzyl alcohol at moderate temperature. The structure and morphology of the resulting particles were characterized by XRD, IR and SEM analysis. The obtained ZnTiO₃ powders showed photocatalytic activity in the degradation of Malachite Green (MG) under UV-light irradiation. The antimicrobial activity of synthesized zinc titanates was investigated towards *Esherihia coli* bacteria.

(Received March 19, 2012; Accepted June 6, 2012)

Keywords: ZnTiO₃, sol-gel methods, photocatalysis, *E. coli*, as a representative species of bacteria

1. Introduction

Zinc titanate ceramics attracts the attention of researchers due to their various applications as paint pigments, sorbents, microwave dielectrics, catalysts, etc. [1,2].

The simultaneous synthesis of a ZnO-TiO₂ composite usually results in the formation of one or more of the three known compounds including Zn₂TiO₄ (zinc orthotitanate), ZnTiO₃ (zinc metatitanate), and the metastable form of zinc metatitanate, Zn₂Ti₃O₈ (cubic) [1-3]. The metastable Zn₂Ti₃O₈ is regarded as a low-temperature form of ZnTiO₃, existing below 820°C. Among these compounds, ilmenite type hexagonal ZnTiO₃ based ceramics has been reported to have superior electrical properties [4]. However, pure zinc metatitanate ZnTiO₃ can not be easily obtained because it decomposes into Zn₂TiO₄ and rutile at temperatures roughly 920-940 °C [2, 4]. The phase transitions of ZnO-TiO₂ system are complex and affected by many factors, such as starting materials and preparation method. Therefore, it is still a challenge to synthesize ZnTiO₃ phase.

Zinc titanates are usually synthesized by conventional solid state reactions at high temperatures [1]. Due to some limitations of solid-state synthesis, such as large grain size and uncontrolled and irregular morphologies, several alternative obtaining methods have been elaborated including mechanochemical activation [5,6], molten salt synthesis [7] and a semi-chemical route combined with vigorous microbeads milling [8,9]. Amongst chemical routes, sol-gel techniques offer important advantages to achieve excellent compositional control, high homogeneity of the products, simple laboratory equipment and, the most significant one, low sintering temperature. Therefore, many efforts have been aimed to produce crystalline ZnTiO₃ at the low crystallisation temperature by sol-gel methods [10-16]. Depending on the solvent used, sol-gel procedures can be aqueous (hydrolytic) and nonaqueous (nonhydrolytic), but the latter is

*Corresponding author: astoy@abv.bg

claimed to be more advantageous and promising in terms of better control over particle size and crystallinity [17]. Although in some cases nonhydrolytic procedures involve the use of hydrated metal oxide precursors, in the current literature the synthesis of metal oxides in organic solvents is typically denoted as “nonhydrolytic” [17].

In our previous work, we reported on aqueous sol-gel synthesis of ZnTiO_3 and its antibacterial properties [18]. The present work continues our investigations on the synthesis of nanosized powders in the ZnO-TiO_2 system [18]. In this paper, the authors have synthesized ZnTiO_3 by aqueous and nonaqueous sol-gel procedures and the team also makes an attempt to compare their photocatalytic and antibacterial properties.

2. Experimental

Materials

The reagents used in this study were titanium tetrachloride and titanium ethoxide (Fluka), citric acid monohydrate, ethylene glycol, HCl, zinc acetate dihydrate and zinc chloride (Sigma-Aldrich), benzyl alcohol ($\geq 99.5\%$), absolute ethanol and diethyl ether from Merck. The dye Malachite Green oxalate ($\text{C}_{46}\text{H}_{50}\text{N}_4 \cdot 3\text{C}_2\text{H}_2\text{O}_4$) was supplied from Sigma. All the chemicals were used without further purification.

Preparation of zinc titanates

For the synthesis of zinc titanate by hydrolytic route zinc acetate and titanium ethoxide were used as starting materials (Figure 1). The precursors were dissolved in ethanol at room temperature under vigorous stirring to achieve complete dissolution and mixed with citric acid, ethylene glycol and HCl, as shown in Figure 1. White xerogel was obtained by drying at 110°C for 5h. The as-obtained xerogel was evaporated, dried and calcined at gradually elevated temperatures from 200 to 500°C in air.

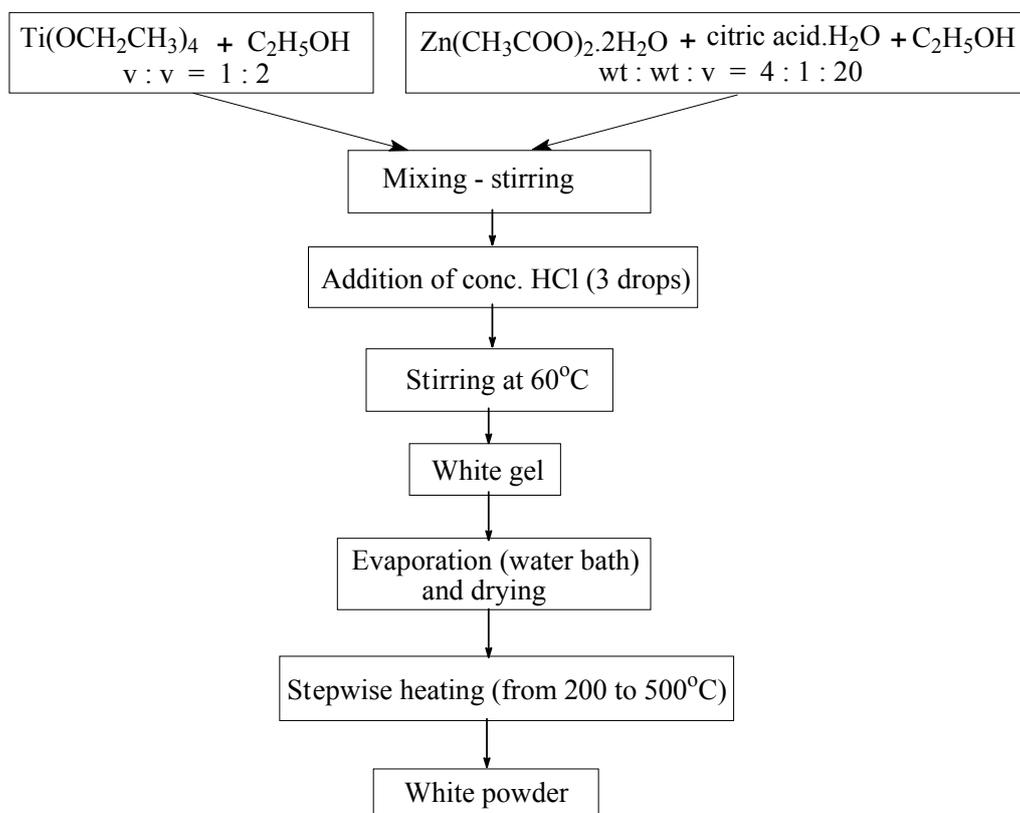


Fig. 1. Scheme of the synthesis of ZnTiO_3 by aqueous sol-gel route - (aq) ZnTiO_3

The synthesis of nanocrystalline ZnTiO_3 by nonaqueous route was based on the reaction between TiCl_4 , ZnCl_2 and benzyl alcohol according to the reaction scheme shown in Figure 2. The

reaction was performed in a regular glass beaker under continuous stirring at 60°C for 8 hours. Thus obtained mixture was left for aging at room temperature for two weeks. The resulting white thick suspension was centrifuged at 5000 rpm for 15 min and the supernatant was discarded by decantation. The white precipitate was then washed two times with absolute ethanol and three times with diethyl ether (1×20 ml). After every washing step, the solvent was separated by centrifugation. The collected material was dried in air overnight and then ground into a fine powder. The obtained powder was calcined at 200-600°C (Figure 2). The molar ratio ZnO/TiO₂ in both synthetic routes was 50:50.

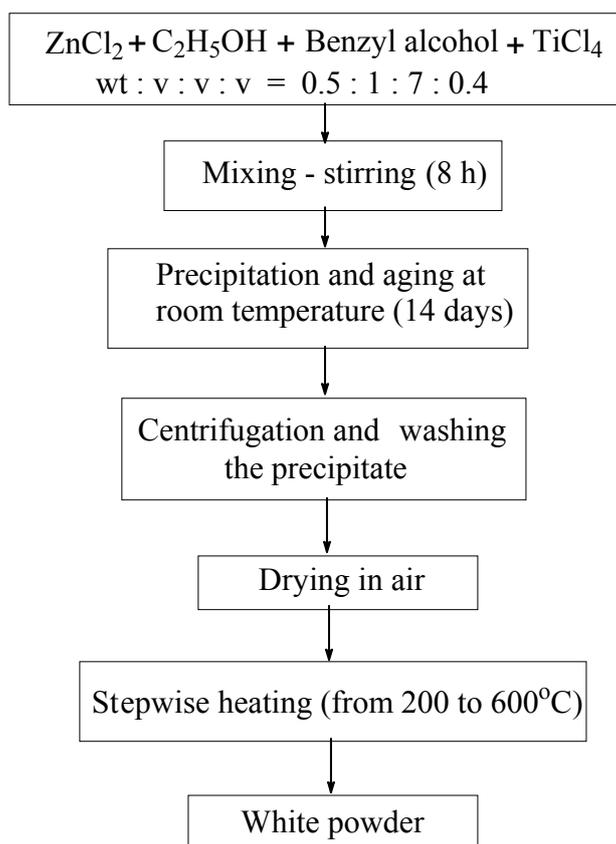


Fig. 2. Scheme of the synthesis of ZnTiO₃ by nonaqueous sol-gel route – (n-aq) ZnTiO₃

The phase formation processes were established by Bruker D8 Advance X-ray apparatus. The morphology of the resulting particles were characterized by SEM (SEM 525M). The main short range orders of the nanosized powders were determined by IR spectroscopy (Nicolet 320 FTIR spectrometer). The optical absorption of the obtained products was measured by UV-Vis analysis (Spectrophotometer Evolution 300).

Photocatalytic activity experiments

The photocatalytic activities of the synthesized powders were evaluated by degradation of a model aqueous solution of Malachite Green (MG). The initial concentration of MG aqueous solution was 5 ppm. In a typical procedure zinc titanate sample (100 mg) was added to 150 ml dye solution to form slurry. After that, the suspension was magnetically stirred in the dark for 15 min to ensure the establishment of an adsorption-desorption equilibrium. Then the above mixture was exposed to UV irradiation by a black light blue UV-lamp (Sylvania BLB 50 Hz 8W T5) with the major fraction of irradiation occurring at 365 nm. All photocatalytic tests were performed at constant stirring (450 rpm) and room temperature of 25°C. At regular time intervals of illumination, aliquot samples (3 mL/each time) were withdrawn and centrifuged in order to remove the solid particles. The dye decoloration was measured by a Jenway 6505 UV-Vis spectrophotometer at 618 nm, the maximum absorption wavelength of MG.

Bactericidal activity measurements

The antimicrobial action of the prepared samples was investigated using *Escherichia coli* (ATCC 25922) with an initial cell density of approximately 10^5 colony forming units (CFU) per ml. The tests were carried out as previously described [18]. The bacterial suspensions with 1 mg/ml of zinc titanates were tested in the dark and in the presence of UV radiation under continuous stirring with magnetic stirrers. UV light irradiation was performed by a black light blue UV-lamp (Sylvania BLB 50 Hz 8W T5). The experiments continued up to 2 hours at 25°C. At regular intervals of time, the definite amounts from any experimental sample were withdrawn and serial dilutions were prepared before plating. The number of viable cells in all samples was determined by spread plate method. After overnight incubation at 37°C the colonies on the plates were counted and results were calculated per 1 ml. The removal efficiency, E , was calculated as:

$$E = \frac{C_i - C_f}{C_i} \times 100$$

C_i and C_f are the initial and final CFU/ml, respectively. Antibacterial effect was evaluated based on the decrease in the colony forming units on agar plates.

3. Results and discussion

Characterization of synthesized powders

The X-ray diffraction patterns of both samples are shown in Figure 3. Zinc titanate (ZnTiO_3 , JCPDS 26-1500) only, was obtained during the aqueous sol-gel (Fig. 3a), while TiO_2 (rutile - JCPDS 89-0555, anatase - JCPDS 78-2486) along with ZnTiO_3 crystallized during the nonaqueous sol-gel processes (Fig. 3b). After heat treatment at 600 and 700°C of both samples, the XRD patterns did not change essentially. The only one difference observed in the XRD pattern of (n-aq) ZnTiO_3 sample is the absence of TiO_2 (anatase) after heat treatment at 700 °C. The average crystallite size of as obtained powders calculated from the broadening of the diffraction line using Sherrer's equation is about 20 nm for (aq) and 40 nm for (n-aq) ZnTiO_3 .

According to SEM observations (Fig. 4) both samples are characterized by a strong tendency to agglomeration with the average particle size of the aggregates about 1 μm . The microprobe analysis showed presence of ZnTiO_3 only (Fig. 4a-aqueous), and ZnTiO_3 along with TiO_2 (anatase) in another sample (Fig. 4b-nonaqueous), which is in good accordance to the XRD results. The UV-Vis absorption spectra are shown in Fig. 5. As it is seen from the figure the absorption decreases after 400 nm. Besides, the (aq) ZnTiO_3 possesses better transparency than those obtained by nonaqueous sol-gel method, probably as a result of its brighter color.

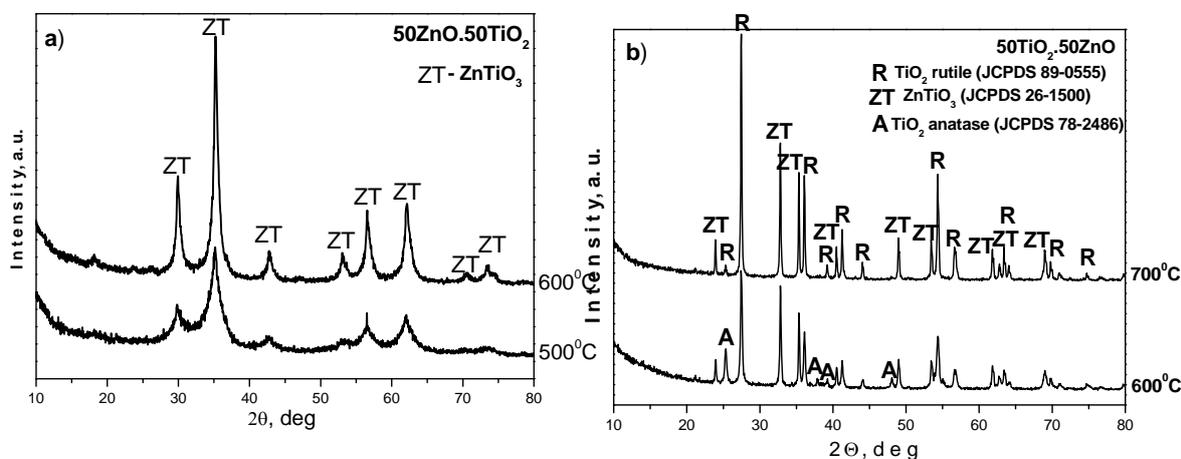


Fig. 3. X-ray diffraction patterns of investigated samples obtained by aqueous and nonaqueous sol-gel methods

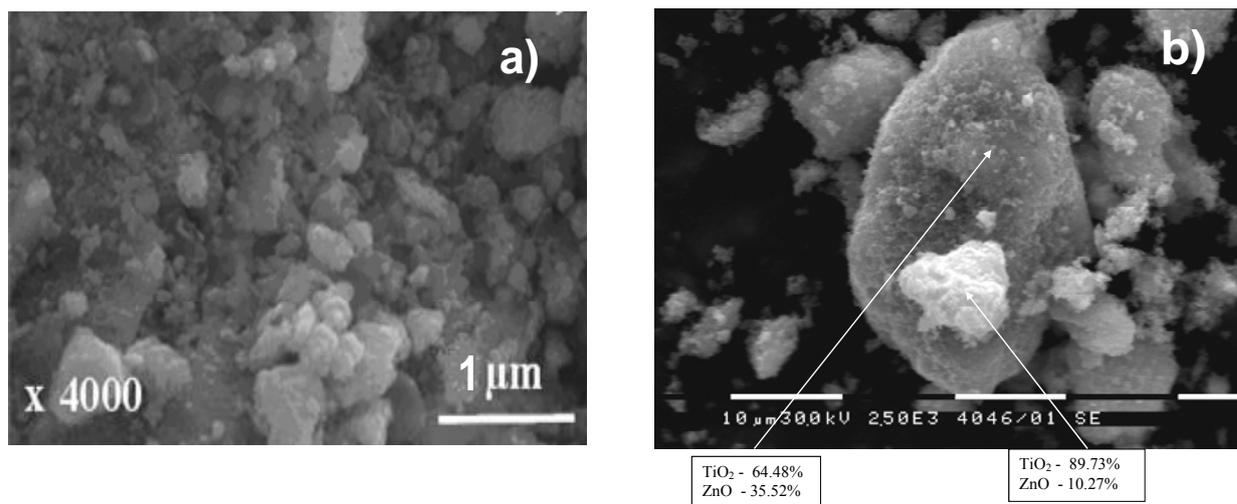


Fig. 4. SEM micrographs of the samples obtained by a) aqueous and b) nonaqueous sol-gel methods

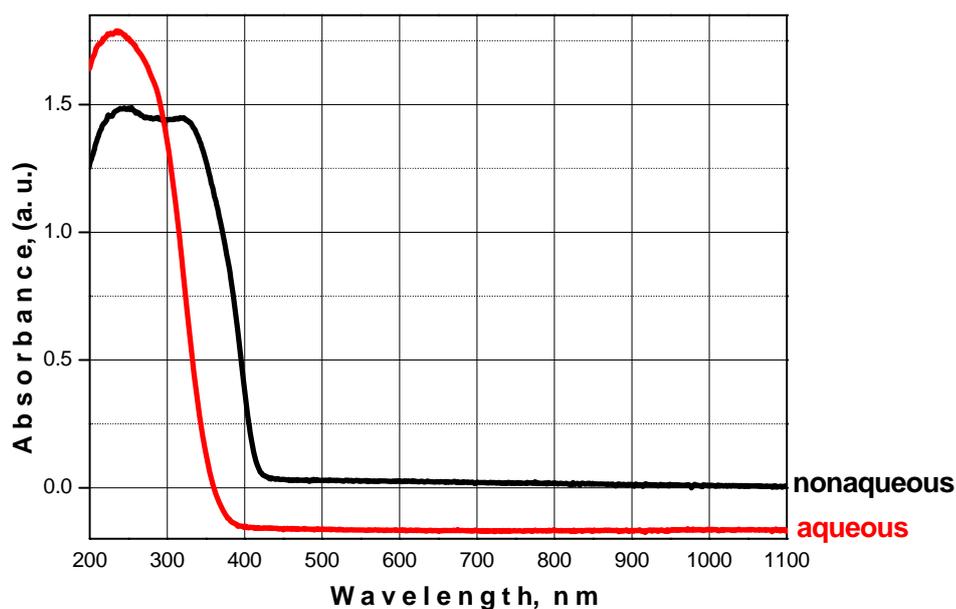


Fig. 5. UV-Vis of ZnTiO_3 obtained by both sol-gel methods

The IR spectra of investigated samples are shown in Figure 6. In the spectra of (aq) ZnTiO_3 , dominant bands at $610, 490 \text{ cm}^{-1}$ along with a weak one at 420 cm^{-1} are observed. It is well known that bands in the absorption range $700\text{-}400 \text{ cm}^{-1}$ could be related to the vibrations of TiO_6 units in ZnTiO_3 [19,20]. As it was mentioned above, according to the X-ray diffraction data for this sample, only one phase (ZnTiO_3) was detected. Besides, it is also known that bands corresponding to ZnO_n polyhedra are in the same absorption range [21,22]. The difference of the IR spectrum of another composition (n-aq ZnTiO_3), is connected to the increased intensity of the band centred at 420 cm^{-1} . As it is known this band is typical for the vibrations of TiO_6 units building up the rutile modification and its presence is in agreement with the X-ray diffraction results [23,24]. The weak band near 450 cm^{-1} could be related to the Ti-O stretching vibrations in ZnTiO_3 [19, 20].

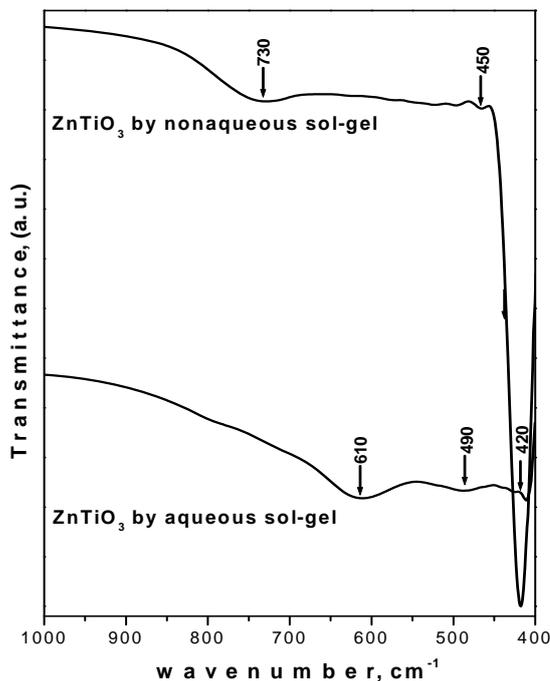


Fig. 6. IR spectra of samples A and B

Photocatalytic activity

The photocatalytic degradation of MG in the presence of titanate samples is shown in Fig. 7. As can be seen, the photocatalytic activity of the synthesized by nonaqueous route zinc titanate (n-aq) was improved in comparison to that prepared by aqueous route (aq). During the time of the test (180 min) there was slight decoloration of MG in the presence of (aq) ZnTiO_3 , while for (n-aq) ZnTiO_3 it completed in 110 min.

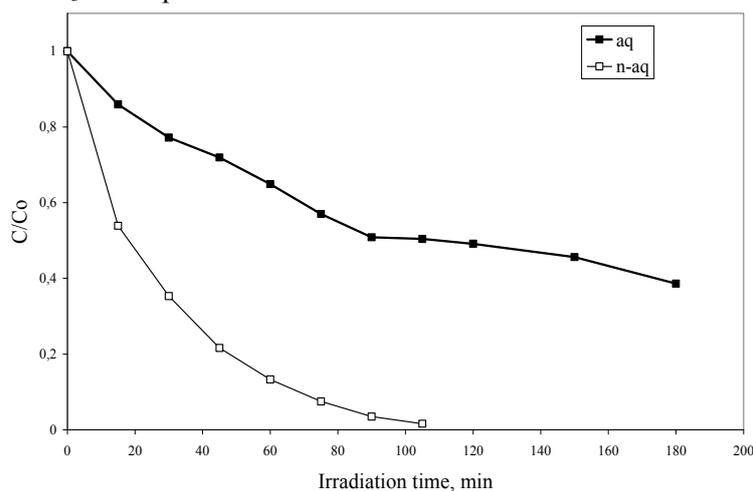


Fig. 7. Photocatalytic degradation of MG by zinc titanates obtained by aqueous (aq) and nonaqueous route (n-aq)

Antibacterial activity

The effect of UV illuminated and non-illuminated (aq) ZnTiO_3 /(n-aq) ZnTiO_3 on removal of *E. coli* is presented at Fig. 8 and 9, respectively. The experiments were done at initial 1.34×10^5 CFU/ml and photocatalyst concentration of 1 mg/ml.

In the presence of UV radiation the 99.6 % removal efficiency of (aq) ZnTiO₃ was achieved in 60 min, whereas in absence of UV light 99.7 % of cells were reduced for 120 min (Fig. 8). Data about (n-aq) ZnTiO₃ showed that at the same initial conditions, in the presence of UV light 99.9 % removal efficiency was 45 min, and in the dark – 97.1 % of bacteria were killed for 120 min (Fig. 9).

Both synthesized powders exhibited good antibacterial activity in the presence of UV-radiation, but the antibacterial activity of (n-aq) ZnTiO₃ was slightly better comparing to that of (aq) ZnTiO₃. The disinfection process for illuminated (n-aq) ZnTiO₃ was virtually completed in 45 min, while the complete killing of bacteria for (aq) ZnTiO₃ was achieved after 90 min. However, during dark studies (aq) ZnTiO₃ and (n-aq) ZnTiO₃ possess similar antibacterial activity: for 120 min viable cell counts were decreased to 0.3 % and 2.9 %, respectively. This can be explained by the above discussed sample composition.

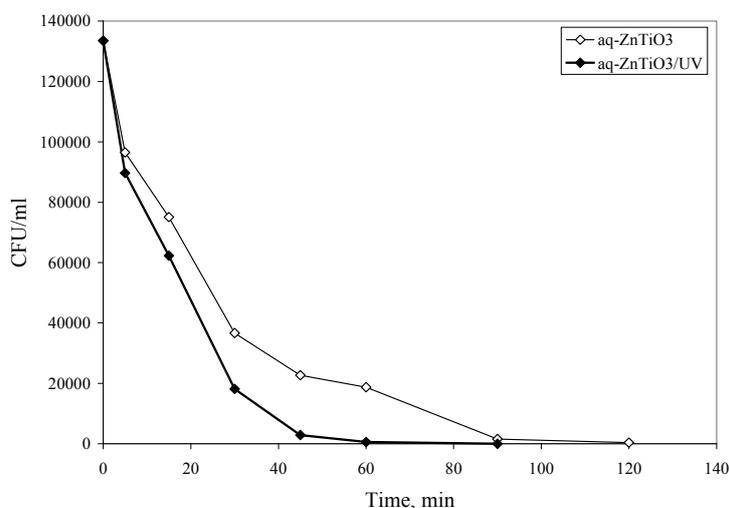


Fig. 8. Removal efficiency of *E. coli* in the presence of (aq) ZnTiO₃

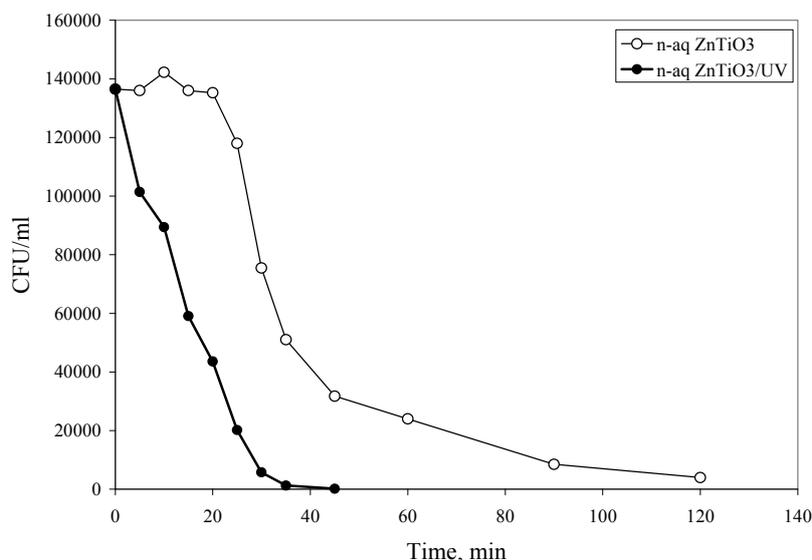


Fig. 9. Removal efficiency of *E. coli* in the presence of (n-aq) ZnTiO₃

4. Conclusions

Nanosized ZnTiO₃ powders were synthesized by hydrolytic and nonhydrolytic sol-gel synthesis. Pure ZnTiO₃ was obtained by aqueous route, while a mixture of ZnTiO₃ and TiO₂ (rutile) was separated using nonaqueous sol-gel method.

Photocatalytic activity of ZnTiO₃ prepared by nonhydrolytic method was improved in comparison to that of ZnTiO₃ prepared by hydrolytic route.

The synthesized powders exhibited good antibacterial activity against *E. coli*. In the experimental conditions the bacterial inactivation with both powders was enhanced by the presence of UV radiation, followed to killing of more than 99% of bacteria within 60 minutes. Our results correlated well with the principle of photocatalytic disinfection activity of metal oxide powders [19,20].

It could be concluded that the synthesized by nonhydrolytic method ZnTiO₃ possesses better photocatalytic and antibacterial properties in comparison to that prepared by hydrolytic route.

References

- [1] Y.S. Chang, Y.H. Chang, I.G. Chen, G.J. Chen, Y.L. Chai, T.H. Fang, S. Wu, *Ceramics International*, **30**, 2183-2189 (2004).
- [2] N.T. Nolan, M.K. Seery, and S.C. Pillai, *Chem. Mater.*, **23**(6), 1496-1504 (2011).
- [3] F.H. Dullin and D.E. Rase, *Phase Equilibria in the System ZnO-TiO₂*, **43**(3), 125-131 (1960).
- [4] Z. Cai, J. Li, Y. Wang, *Journal of Alloys and Compounds*, **489**, 167-169 (2010).
- [5] P. M. Botta, E. F. Aglietti and J. M. Porto López, *Journal of Materials Science*, **39**, 5195-5199 (2004).
- [6] N. Labus, N. Obradović, T. Srećković, V. Mitić, M.M. Ristić, *Science of Sintering*, **37**, 115-122 (2005).
- [7] X. Xing, C. Zhang, L. Qiao, G. Liu, J. Meng, *Journal of the American Ceramic Society*, **89**(3), 1150-1152 (2006).
- [8] H.T. Kim, S.H. Kim, S. Nahm, J.D. Byun, Y.H. Kim, *Journal of the American Ceramic Society*, **82**, 3043-3048 (1999).
- [9] X. Liu, F. Gao, L. Zhao, M. Zhao, C. Tian, Effects of V₂O₅ addition on the phase-structure and dielectric properties of zinc titanate ceramics, *Journal of Electroceramics*, **18**, 103-109 (2007).
- [10] Y.S. Chang, Y.H. Chang, I.G. Chen, G.J. Chai, Y.L. Chai, *J. Cryst. Growth*, **243**, 319-326 (2002).
- [11] L. Zhao, F. Liu, X. Wang, Z. Zhang and J. Yan, *Journal of Sol-Gel Science and Technology*, **33**, 103-106 (2005).
- [12] A. R. Phani and S. Santucci, *Journal of Materials Science Letters*, **20**, 573-575 (2001).
- [13] L. Hou, Y. D. Hou, M. K. Zhu, J. Tang, J. B. Liu, H. Wang, and H. Yan, *Materials Letters*, **59**, 197-200 (2005).
- [14] A. R. Phani, M. Passacantando and S. Santucci, *Journal of Physics and Chemistry of Solids*, **68**, 317-323 (2007).
- [15] Y. L. Chai, Y. S. Chang, G. J. Chen and Y. J. Hsiao, *Materials Research Bulletin*, **43**, 1066-1073 (2008).
- [16] A. Shalaby, Y. Dimitriev, R. Iordanova, A. Bachvarova-Nedelcheva, Tz. Iliev, *Journal of the University of Chemical Technology and Metallurgy*, **46**(2), 137-142 (2011).
- [17] M. Niederberger, N. Pina, *Metal Oxide Nanoparticles in Organic Solvents*, Springer, 2009, 7-16.
- [18] A. Stoyanova, Y. Dimitriev, A. Shalaby, A. Bachvarova-Nedelcheva, R. Iordanova, M. Sredkova, *Journal of Optoelectronics and Biomedical Materials*, **3**(1), 24-29 (2011).
- [19] O. Yamaguchi, M. Morimi, H. Kawabata, et al., *J. Amer. Ceram. Soc.*, **70**, c97-8 (1987).
- [20] B. G. Shabalin, *Mineral. Zh.*, **4**, 54-61 (1982).
- [21] M. Mancheva, R. Iordanova, Y. Dimitriev, *J. Alloys Compd*, **509**(1), 15-20 (2011).
- [22] M. Andres-Verges, M. Martinez-Gailego, *J. Mater. Sci.*, **27**, 3756-62 (1992).
- [23] A. Murashkevich, A. Lavitkaya, T. Barannikova et al., „Infrared absorption spectra and structure of TiO₂-SiO₂ composites“, *J. Appl. Spectr.*, **75** (5), 2008, 730-734.
- [24] E. Yurchenko, G. Kustovar, S. Bacanov, „Vibrational spectroscopy of inorganic compounds“, Nauka 1981 (in Russian).