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Investigation of the photocatalytic activity and radiopacity of nanopowders produced by pulsed electron beam evaporation in vacuum

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Abstract. In this work, were investigated the photocatalytic properties and radiopacity of titanium TiO_2 and zinc oxide Zn-ZnO nanopowders produced by the pulsed electron beam evaporation method in vacuum. Photocatalytic activity was measured based on the rate of decomposition of methyl violet by nanoparticles of various concentrations under the action of UV radiation. Radiopacity was evaluated by comparing the X-ray attenuation coefficients with Na-CMC buffer solution containing NPs test compounds and commercial iodine computer tomography contrast agent Ultravist®. In both cases, the NPs of zinc compounds showed more pronounced properties by accelerating the photodegradation reaction by 1.6 times, relative to the control sample and showing a attenuation factor of 70% of Ultravist®.

Keywords: nanoparticles, zinc oxide, titanium oxide, photocatalysis, radiopacity.

1. Introduction

Currently, many works are emerging on the study of nanomaterials. Unlike bulk substances, when transitioning to a nanoscale state, some compounds significantly enhance and sometimes even change their properties. Of great interest to the studies are nanoparticles (NPs) of titanium oxide (TiO_2) and zinc (ZnO) for use as photocatalysts as well as radiopaque agents.

The photocatalytic activity of these compounds is well known [1], and can be used for surface self-cleaning, water and air purification, solar panels, in various devices and sensors. The exhibition of photocatalytic properties of described compounds appears due to the peculiarities of their electronic structure, in particular, the existence of a valence band of conductivity in them. Nanoparticles of zinc and titanium oxide often act as photocatalysts, thin coatings, nanoparticles of which have antimicrobial and bactericidal properties [2]. However, various methods for producing nanopowders can significantly affect their properties. As an example, bismuth oxide and zirconium nanopowders produced by pulsed electron beam evaporation (PEBE) method showed high biological and photocatalytic activity [3].

The use of NPs as radiocontrast agents can greatly enhance the capabilities of radiography methods, especially computed tomography (CT). The development of ferromagnetic properties of NPs zinc [4] and titanium oxide [5], including alloyed with 3-d metal ions, is reported. This makes it possible to control the location of particles in the area of interest using an external magnetic field, which greatly simplifies the visualization of individual organs. Moreover, it is possible to create antibody-conjugated nanoparticles [6], which makes these compounds trope to individual cells or tissues, which also directly affects the effectiveness of CT.

2. Materials and methods

2.1. Nanoparticles

The study examined NPs titanium oxide (TiO_2) and zinc oxide (ZnO-Zn) produced by PEBE method in vacuum [7]. This method makes it possible to produce small NPs with a high specific surface area. This provides a high reactivity of the tested NPs. In addition, an important feature of this method is the formation of a significant number of defects of various types, which affects the manifestation of magnetic, luminescent and other properties.

2.2. Photocatalytic activity

The method for evaluating the photocatalytic properties of nanopowders was as follows: methyl violet (MV) dye was dissolved in distilled water to obtain the concentration of 10 μg/mL. Then, an aqueous suspension of the test NP of 300 μl (for NP concentration of 100 μg/mL) consisting of 10 mg NP and 5 mL distilled water and 300 μl (for NP concentration of 300 μg/mL) consisting of 20 mg NP and 5 mL distilled water was added to the solution. The control sample did not contain NPs. The suspension was then irradiated on a UV gas discharge lamp DRS 250-3 for 40 minutes. The absorbance of the solution was measured every 5 minutes to determine the rate of discoloration of the solution. To do this, an aliquot of 4 ml of each solution was taken into a quartz cuvette and placed in an "Ekroschim PE-5400UF" spectrophotometer. Absorbance measurements were performed at a wavelength of 595 nm before and after irradiation by the UV radiation.

2.3. Radiopacity

The radiopacity of the studied NPs was evaluated relative to commercial iodine CT contrast agent Ultravist®, by analogy with the work [8]. An aqueous solution of carboxymethylcellulose sodium salt (Na-CMC) of 0.24 g Na-CMC per 30 ml of water was used as the basis for creating contrast samples with TiO_2 and ZnO-Zn. Suspensions of TiO_2 and ZnO-Zn were added to the resulting mixture to produce final NPs concentrations of 2.5, 5, 12.5%. Distilled water and Ultravist® were used as control samples.

During the work were obtained X-ray images of the test samples. The X-ray diagnostic device "Yasen-01" was used for the investigation. Radiograms were obtained using a flat-panel digital detector. The X-ray attenuation of the samples was analyzed by the brightness of the obtained images. Based on the measurements were estimated linear X-ray attenuation coefficients. Image processing was performed in the "ImageJ" software package.

3. Results and discussion

3.1. Photocatalytic activity measurement

The dependence of the rate of discoloration of the MV solution on the time of exposure to UV radiation can be described by the linear equation $y = kx + b$. The value of the photodegradation velocity is determined by the tangent of the angle of inclination of the straight line, that is, by the coefficient k. In this case, the larger the modulus of the value of this coefficient, the faster the photodetection reaction proceeds [9].

During the experiment, a change in the optical density of the test samples was observed as a result of photodegradation of the dye. The ratio of the absorbance of irradiated with UV radiation samples C and absorbance of the samples before irradiation C_0 was used. The measurement results for the NPs concentration of 300 μg/mL are shown in Fig.1.

To find the coefficient k, the obtained values were approximated and summarized in Table 1.

Table 1. The k coefficient values for 300 mcg/ml TiO_2 and ZnO-Zn NP

Sample	k absolute value	Relative to control
Control	0.0053	1
TiO_2	0.0078	1.47
Zn-ZnO	0.0085	1.60

The obtained values indicate the presence of pronounced photocatalytic abilities of the studied NPs. At the same time, the highest photocatalytic activity was shown by the NPs of the zinc compound, accelerating the photodegradation reaction by 1.6 times, relative to the control sample.

However, the degradation efficiency of the MV of the studied NPs is lower than that of the TiO_2 and ZnO compounds considered in other works [10, 11]. Is reported 30 and 45 percent degradation of MV in 40 minutes of UV radiation by NPs TiO_2 and ZnO photocatalysts, respectively.

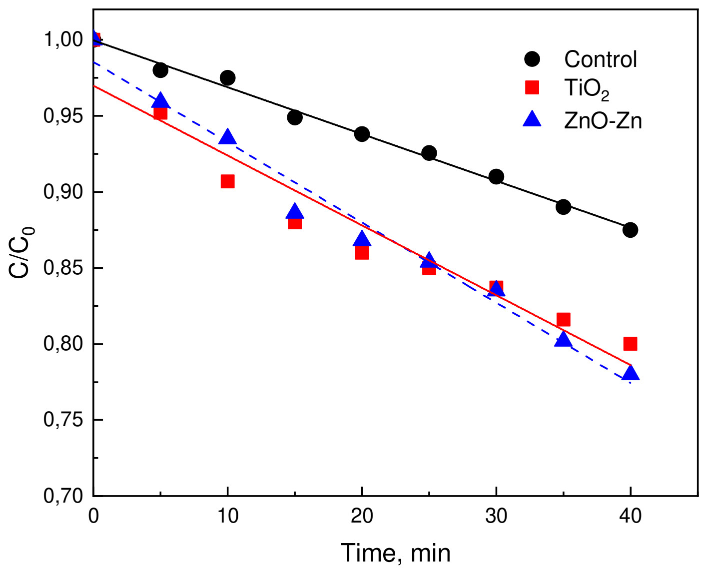

Fig.1. Relative optical density of 300 mcg/ml TiO_2 and ZnO-Zn samples compared to control.

3.2. Radiopacity measurement

X-rays of the test samples containing NPs titanium oxide and zinc oxide are shown in Figs.2 and 3, respectively.

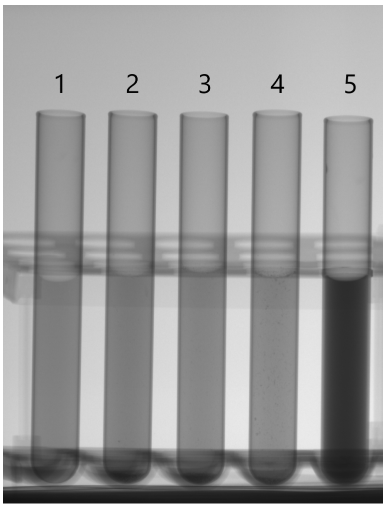

Fig.2. Radiogram of TiO_2 containing samples (1– water, 2– 12.5 %, 3– 5 %, 4– 2.5 %, 5– Ultravist).

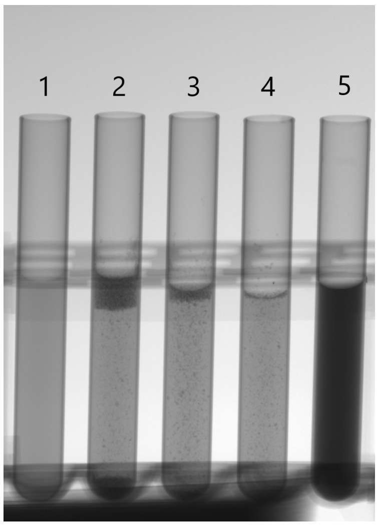

Fig.3. Radiogram of ZnO-Zn containing samples (1– water, 2– 12.5 %, 3– 5 %, 4– 2.5 %, 5– Ultravist).

Fig.2 shows that the TiO_2 NPs showed no radiopaque ability, comparing with distilled water. At the same time the zinc compound sample (Fig. 3) absorbs X-ray radiation only in the agglomeration. The highest attenuation coefficient was found in the sample containing 12.5% NPs ZnO-Zn and amounted to ~70% of the Ultravist® medical X-ray contrast. However, this value was obtained only in the field of formation of NPs agglomerations. The formation of large accumulations of NPs when working with a bio-object is undesirable, which means that this effect cannot be used in CT, but it can be used in other areas of radiography.

4. Conclusion

According to the results of the study, it can be concluded that ZnO-Zn zinc oxide NPs exhibits more pronounced properties as a photocatalyst and as a radiopaque agent than TiO_2 titanium oxide NPs.

Measurement of the photocatalytic activity of the examined NPs showed the presence of the effect of accelerated photodegradation under the action of UV radiation in both compounds. The reactivity was lower compared to similar experiments, but the photocatalytic activity of NPs TiO_2 and ZnO-Zn can be increased by conducting experiments on doping or annealing these nanopowders [12].

The experiment using TiO_2 and ZnO-Zn as radiopaque agents showed no significant results. The effective atomic number of these compounds is lower than that of iodine, the main component of most radiopaque agents, including Ultravist®, which implies a low ability to attenuate X-ray radiation. However, 70% attenuation was achieved with relating to the medical radiopaque contrast in the ZnO-Zn NPs agglomeration.

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5. References

[1] Ong C.B., Ng L.Y., Mohammad A.W., *Ren. and Sus. Ener. Rev.*, **81**, 536, 2018; doi: 10.1016/j.rser.2017.08.020

[2] Pang S., He Y., Zhong R., Guo Z., He P., Zhou C., *Ceramics Int.*, **45**(10), 12663, 2019; doi: 10.1016/j.ceramint.2019.03.076

[3] Svetlova O.A., Sokovnin S.Y., Il'ves V., *J. Phys.: Conf. Ser.*, **2064**(1), 012087, 2021; doi: 10.1088/1742-6596/2064/1/012087

[4] Il'ves V.G., Sokovnin S.Y., *Phys. of the Sol. St.*, **56**(11), 2273, 2014; doi: 10.1134/S1063783414110110

[5] Santara B., Pal B., Giri P. K., *J. of app. phys.*, **110**(11), 114322, 2011, doi: 10.1063/1.3665883

[6] Kim G.C., Kim G.J., Park S.R., Jeon S.M., Seo H.J., Iza F., Lee J.K, *J. of Phys. D: App. Phys*., **42**(3), 032005, 2008; doi: 10.1088/0022-3727/42/3/032005

[7] Sokovnin S.Y., Il'ves V.G., Zuev M.G., *Eng. of Nanobiomat.*, **2**, 29, 2016; doi: 10.1016/B978-0-323-41532-3.00002-6

[8] Ghazanfari A., Marasini S., Miao X., Park J.A., Jung K.H., Ahmad M.Y., *Coll. and Surf. A: Phys. Chem. and Eng. Aspects*, **576**(5), 73, 2019; doi: 10.1016/j.colsurfa.2019.05.033

[9] Sokovnin S.Y., Il'ves V.G., Malova O.A., Kiseleva M.A., Ulitko M.V., Sultanova T.R., *J. Phys.: Conf. Ser.*, **1954**(1), 012047, 2021; doi: 10.1088/1742-6596/1954/1/012047

[10] Zulmajdi S.L.N., Zamri N.I.I., Yasin H.M., Kusrini E., Hobley J., and Usman A., *React. Kin., Mech. and Catal.,* **129**(1), 519, 2020; doi: 10.1007/s11144-019-01701-x

[11] Rajapriya M., Sharmili S.A., Baskar R., Balaji R., Alharbi N.S., Kadaikunnan S., *J. of Cluster Sci.*, **31**(4), 791, 2020; doi: 10.1007/s10876-019-01686-6

[12] Senthilkumar S., Ashok M., Kashinath L., Sanjeeviraja C., Rajendran A., *Smart Sci*, **6**(1), 1, 2018; doi: 10.1080/23080477.2017.1410012