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Synthesis and photocatalytic performance of Fe (III), N co-doped TiO_2 nanoparticles

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Fe(III), N-TiO_2 nanoparticles were synthesized at low temperature via nonhydrolytic sol-gel method. The present work continues our investigations on the synthesis of nanosized TiO_2 powders with improved photocatalytic activity. The structure and morphology of the obtained samples was characterized by XRD, IR and UV-Vis spectroscopy. The average crystallite size of as prepared Fe and N co-doped TiO_2 was about 15–20 nm. The photocatalytic activity of doped TiO_2 powders was studied in UV and visible light and was evaluated by the degradation of Malachite Green (MG) as model pollutant. The relationship between dopant concentration and photocatalytic activity has been revealed.

Key words: Fe, N-co-doped titanium dioxide, sol-gel, photocatalytic activity.

INTRODUCTION

The application of titanium dioxide photocatalyst for degradation of pollutants has been extensively studied during the past decades owing to its ability to mineralize harmful organic compounds to CO_2 and H_2O under UV (Vis) irradiation. An important drawback of pure TiO_2 is its wide band gap, which allows photoactivation only under UV light irradiation, and quick recombination of electron-hole pairs.

In order to improve the photocatalytic functionality, many attempts have been made by doping of TiO_2 with transition metals.

Among various metal ions, Fe(III) ion has been known to be an effective dopant. Our investigations on the photocatalytic behavior of iron-doped titanium dioxide, prepared by a nonhydrolytic sol-gel method, showed beneficial effect of doping with small amounts of iron [1, 2].

Recently, doping with p-block (N, F, C, S) elements has attracted much attention because it is suggested that the introducing of such elements in the crystal lattice can improve the photo-absorption properties of TiO_2 under visible light illumination [3–5].

On the other hand, it has been reported, that the photocatalytic activity of TiO_2 doped with elements such as sulfur and nitrogen can be further increased by the presence of Fe(III) as a co-dopant [6–10]. Nanocomposite Fe-N-TiO_2 was synthesized and successfully used for inactivation of tumor cells [11].

The present work reports on synthesis of nitrogen- and iron-nitrogen co-doped TiO_2 powders at low temperature using non-hydrolytic sol-gel method. The structure of the obtained samples was characterized by XRD, IR and UV-Vis spectroscopy. The photocatalytic activity of doped TiO_2 powders was studied under both UV and visible light and was evaluated by the degradation of Malachite Green (MG) as a model pollutant.

EXPERIMENTAL

Materials

Titanium(IV) chloride (purity ≥99.0%) was purchased from Fluka, benzyl alcohol (≥99.5%) from Merck, iron(III) nitrate, Malachite Green oxalate ($C_{46}H_{50}N_4.3C_2H_2O_4$), absolute ethanol and diethyl

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ether were supplied by Sigma-Aldrich. All the chemicals were used without further purification.

Preparation and characterization of titania catalysts

It is well known that the doping effect depends on many factors such as synthesis conditions, doping method and the dopant concentration [12, 13]. Pure and doped by Fe and N nanosized TiO_2 were synthesized by a nonhydrolytic sol-gel route from $TiCl_4$ and benzyl alcohol at moderate temperature. In a typical procedure, at first, the dopants were introduced to benzyl alcohol by adding proper amount iron (III) nitrate and urea (1.3 mol%), dissolved in ethanol (Fig. 1). Then, titanium tetrachloride was slowly added to a beaker containing the above mentioned mixture under vigorous stirring. The resulting sols were heated at 60 °C under continuous stirring. The reaction mixtures were left for aging at room temperature until white precipitate was observed. The resulting white thick suspensions were centrifuged at 5000 rpm for 15 min and the supernatant was discarded by decantation. The precipitates were then washed with absolute ethanol and diethyl ether. 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 powders were calcinated at 500 °C for 2 hours. The as-prepared samples are denoted as TiO_2/N for N-doped and TiO_2/*x*%Fe/N for Fe,N-co-doped titania, where *x* represents the Fe/Ti mol ratio.

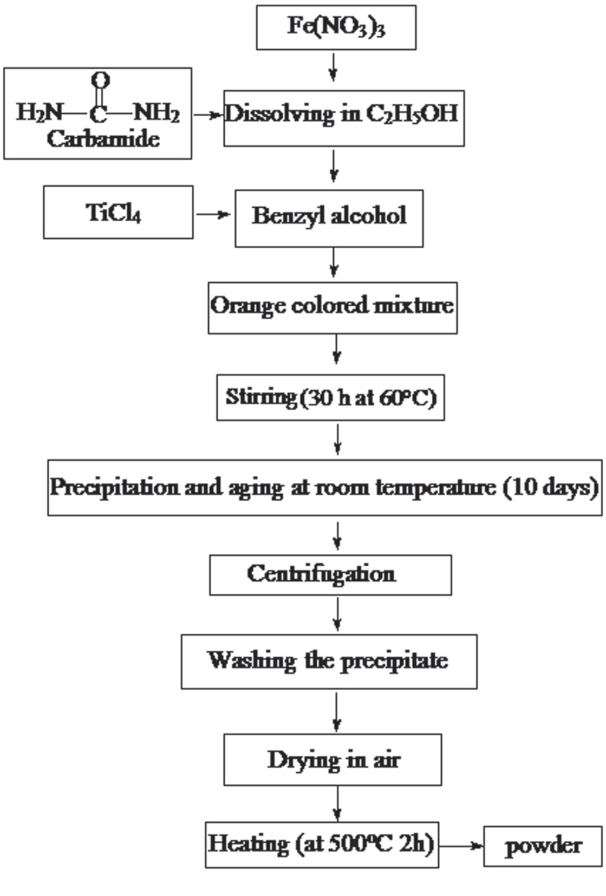

Fig. 1. Scheme of the nonhydrolytic sol-gel synthesis

The phase transformations and structure of the resulting particles were characterized by X-ray diffraction (XRD, Bruker D8 Advance X-ray apparatus) and infrared (IR, using the KBr pellets method (Nicolet-320, FTIR spectrometer with a resolution of ±1cm^{-1}, by collecting 64 scans in the range 1000–400 cm^{-1}). The optical absorption spectra of the powdered samples in the wavelength range 200–500 nm were recorded by a UV–VIS diffused reflectance Spectrophotometer "Evolution 300" using a magnesium oxide reflectance standard as the baseline. The absorption edge and the optical band gap were determined following Dharma et al. instructions [14]. The bandgap energies (E_g) of the samples were calculated by the Planck's equation:

$$E_g = \frac{h.c}{\lambda} = \frac{1240}{\lambda},$$

where Eg is the bandgap energy (eV), h is the Planck's constant, c is the light velocity (m/s), and λ is the wavelength (nm).

Photocatalytic activity experiments

The photocatalytic performance of the synthesized powders was evaluated by degradation of a model aqueous solution of Malachite Green (MG) under UV-Vis irradiation. The initial concentration of MG aqueous solution was 5 ppm. The photocatalyst sample (100 mg) was added to 150 ml dye solution to form slurry. After that, the suspension was magnetically stirred in the dark for 30 min to ensure the establishment of an adsorption-desorption equilibrium. The UV-irradiation source was a black light blue UV-lamp (Sylvania BLB 50 Hz 8W T5) with the major fraction of irradiation occurring at 365 nm. The intensity of UV-light reaching the surface of the suspension was measured with a numeric Luxmeter (LM 37, Dostmann electronic). The mean value of the radiation power impinging on the reacting suspension was estimated to be about 150 Lx.

The visible light source was a 500 W halogen lamp (Sylvania) fixed at 40 cm above the treated solution. The mean value of the radiation power reaching on the suspension was estimated to be about 14000 Lx.

All photocatalytic tests were performed at constant stirring (400 rpm) at room temperature of 25 °C. Aliquot samples (3 mL) of the mixture were taken at regular time intervals and the catalyst was separated through centrifugation (5000 rpm, 15 min). The absorbances of clear aliquots were measured by a Jenway 6505 UV-Vis spectrophotometer at 618 nm, the maximum absorption wavelength of MG.

RESULTS AND DISCUSSION

Characterization of titania samples

The XRD patterns of the Fe and N co-doped TiO_2 are shown in Figure 2. As is seen in the figure, dominate crystalline phase detected in the XRD patterns is anatase (TiO_2) (JCPDS 78-2486). It is noteworthy that in the XRD patterns of samples TiO_2/0%Fe/N, TiO_2/0.5%Fe/N and TiO_2/2%Fe/N small amount of rutile was observed as well. Obviously, the Fe and N co-doping enhances the crystallization of rutile and as a result it appears at lower temperatures (500 °C). It has to be noticed that iron was not found in the XRD patterns of the investigated samples. For comparison, our results are in good accordance with those obtained by other authors [15]. The average crystallite size of as prepared Fe and N co-doped TiO_2 calculated from the broadening of the diffraction line using Sherrer's formula is about 15–20 nm. Obviously, the Fe/N co-doping of TiO_2 did not influence on the particles size. For comparison, the particle size of pure TiO_2 obtained by non-hydrolytic sol-gel method is ~20 nm [1]. Our results differ from those obtained by Songkhum et al. [15], where they established that Fe, N co-doping led to increasing of the crystallite size of the obtained products. Probably, the reason of this discrepancy is due to the used precursors; experimental conditions as well as to the applied non-hydrolytic sol-gel method of synthesis.

The short range order of the obtained Fe/N co-doped TiO_2 submicron powders as well as of undoped TiO_2 is investigated by IR spectroscopy in the range 1000–400 cm^{-1} (Fig. 3). Vibrations of the inorganic building units only were recognized. Bands in the range 470–420 cm^{-1} and 700–600 cm^{-1} are observed which could be related to the vibrations

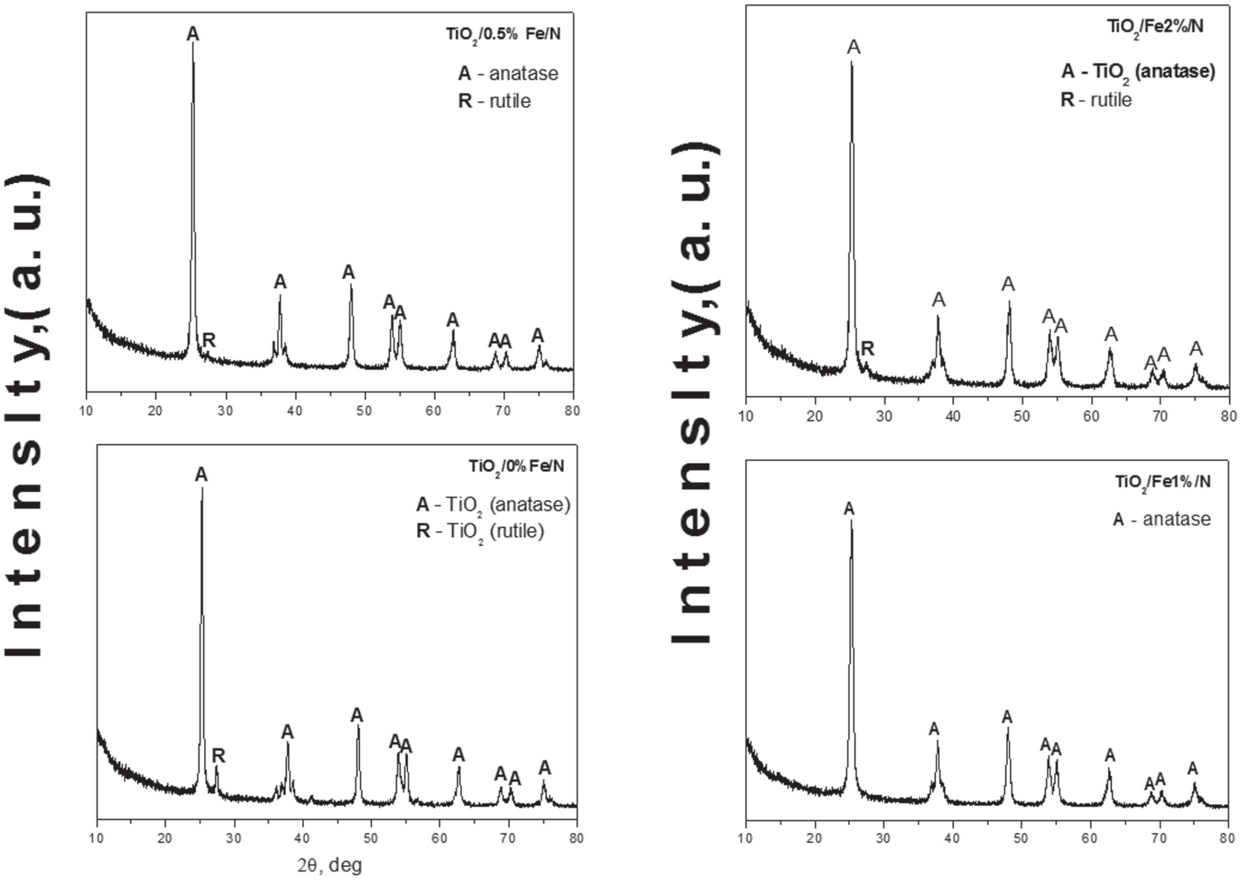

Fig. 2. XRD patterns of Fe/N co-doped TiO_2

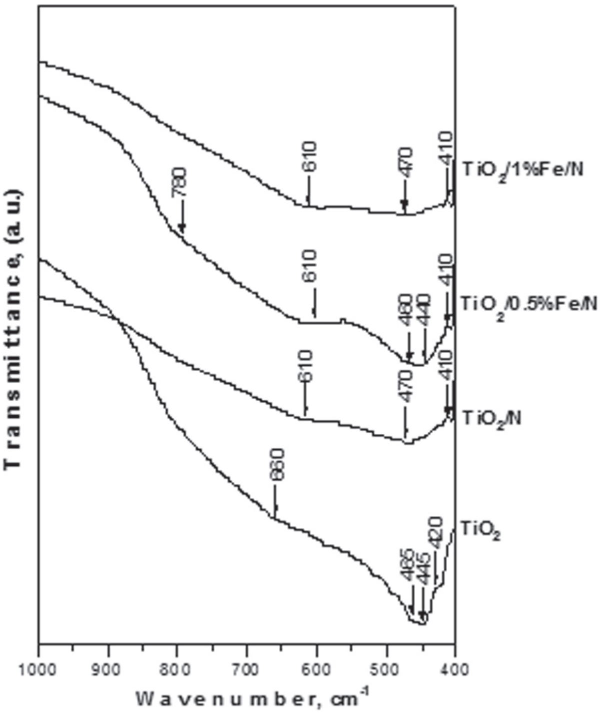

Fig. 3. IR spectra of Fe/N co-doped TiO$_2$ samples

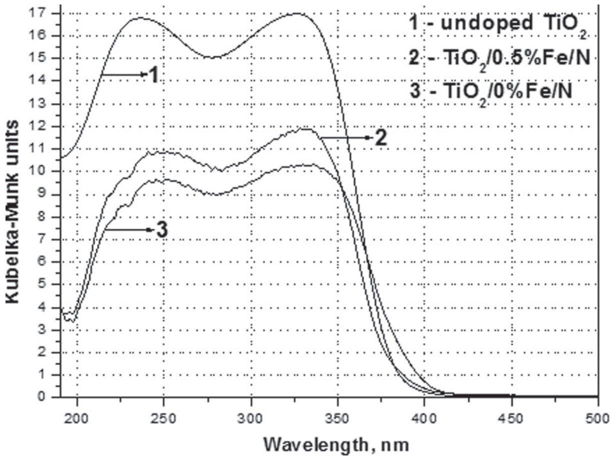

Fig. 4. Uv-Vis spectra of Fe/N co-doped TiO$_2$ samples

Table 1. Cut-off and optical band gap values for obtained compositions

N	Sample	Cut-off, nm	Eg, eV
1.	undoped TiO$_2$	388.33	3.19
2.	TiO$_2$/0%Fe/N	403.26	3.07
3.	TiO$_2$/0.5%Fe/N	386.95	3.2

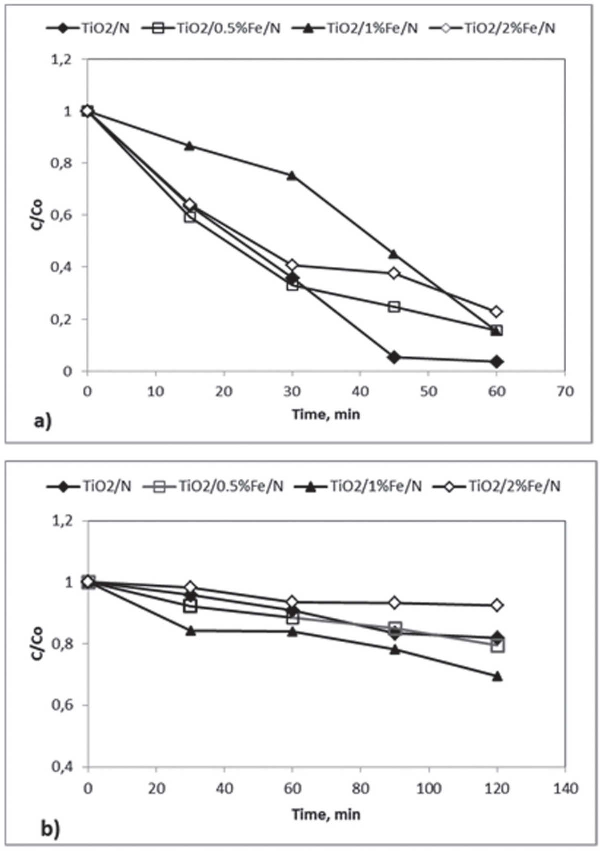

Fig. 5. Photocatalytic activity of Fe/N-modified samples under a) UV irradiation and b) Vis irradiation

of TiO$_6$ units [16, 17]. Despite the fact that iron was not detected in the XRD patterns, its presence was registered by IR spectroscopy (bands in the range 680–470 cm^{-1}). The doping with iron and nitrogen resulted to the appearance of a broad band centred at about 610 cm^{-1}, that could be assigned to the vibrations of FeO$_n$ structural units [18]. Obviously, it is difficult to distinguish the vibrations of TiO$_6$ and FeO$_n$ structural units due to their overlapping.

UV-Visible spectra of the synthesized samples show an absorption edge in the 388–403 nm region. Figure 4 shows the UV-visible absorption of the modified TiO$_2$ compared to that of the undoped and obtained by a nonhydrolytic sol-gel method TiO$_2$. The absorption spectra of the sample TiO$_2$/0.5%Fe/N exhibited a blue shift (Table 1). Obviously, N and/or Fe doping did not lead to a significant shift of the absorption edge or change in energy band gap compared to those of the synthesized pure TiO$_2$. Our results are in accordance with the data obtained by other authors [18]. The calculated energy band gaps of all samples are also shown in Table 1.

Photocatalytic activity

The prepared TiO$_2$ photocatalysts were used to degrade Malachite Green (MG) as a model pollutant under UV-Vis light irradiation and the results were presented in Figures 5a and 5b. The dye MG is widely used in food and textile industries, but it can cause carcinogenic and genotoxic effects on living organisms [19].

Only 6.2% of MG under UV irradiation and 4.7% under visible light irradiation were removed after 180 min photolysis in the absence of catalyst, determining that decoloration was conducted primarily by the photocatalytic process.

As can be seen (Fig. 5), the photocatalytic activity of Fe, N-modified samples under UV irradiation was not improved, comparing to N-modified TiO_2. In the presence of visible light the highest photosensitivity showed TiO_2 modified with 1 mol% Fe and N (Fig. 5). According to the literature, the doped Fe ions can form new energy level below the conduction band of TiO_2 and the N doping either decreases the band gap or creates an N-induced mid-gap level, which can improve the utilization of visible light by the TiO_2 [20].

CONCLUSIONS

Pure and doped by Fe and N nanosized TiO_2 powders (15–20 nm) were synthesized by a nonhydrolytic sol-gel route. According to XRD patterns, mainly TiO_2 (anatase) crystallized. The short range order was verified by IR spectroscopy and presence of TiO_6 (470-420 cm^{-1}), and FeO_n (610 cm^{-1}) building units was proved. Co-doping with Fe and N did not change photocatalytic activity under UV light illumination, comparing to N-modified TiO_2. In the presence of visible light, the highest photo-sensitivity showed the TiO_2 modified with 1% Fe and N.

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REFERENCES

1. A. M. Stoyanova, H. Y. Hitkova, N. K. Ivanova, A. D. Bachvarova-Nedelcheva, R. S. Iordanova, M. P. Sredkova, *Bulg. Chem. Commun.*, **45**(4), 497 (2013).
2. A. Stoyanova, N. Ivanova, R. Iordanova, A. Bachvarova-Nedelcheva, *Nanosci. & Nanotechnol.*, 13, 166 (2013).
3. F. Han, V. S. R. Kambala, M. Srinivasan, D. Rajarathnam, R. Naidu, *Appl. Catal. A*, **359**, 25 (2009).
4. U .G. Akpan, B.H. Hameed, *Appl. Catal. A*, **375**, 1 (2010).
5. M. V. Dozzi, E. Selli, *J. Photochem. Photobiol. C: Photochem. Rev.*, **14**, 13 (2013).
6. P. Xu, T. Xu, J. Lu, S. Gao, N.S. Hosmane, B. Huang, Y. Dai, Y. Wang, *Energy Environ. Sci.*, **9**, 1128 (2010).
7. Y. Cong, J. Zhang, F. Chen, M. Anpo, D. He, *J. Phys. Chem. C*, **111**, 10618 (2007).
8. J. Zhang, Y. Wu, M. Xing, S. A. K. Leghari, S. Sajjad, *Energy Environ. Sci.*, **3**(6), 715 (2010).
9. X. Qiu, Y. Zhao, C. Burda, *Adv. Mater.*, **19**(22), 3995 (2007).
10. X. H. Li, J. B. Lu, Y. Dai, M. Guo, B.B. Huang, *Int. J. Photoenergy*, **2012**, 8 (2012).
11. K. Huang, L. Chen, J. Xiong, M. Liao*, Int. J. Photoenergy*, 2012, 9 (2012).
12. P. Yang, C. Lu, N. Hua, Y. Du, *Mat. Lett.*, **57**(4), 794 (2002).
13. W. K. Choi, A. Termin, M. R. Hoffmann*, J. Phys. Chem*., **98**(51), 13669 (1994).
14. J. Dharma, A. Pisal, Perkin Elmer Inc., Application note.
15. P. Songkhum, J. Tantirungrotechai, *Pure and Applied Chemistry International Conference (PACCON2011)*, 437 (2011).
16. A. N. Murashkevich, A. S. Lavitskaya, T. I. Barannikova, I. M. Zharskii, *J. Appl. Spectr.*, **75**(5), 730 (2008).
17. A. M. Stoyanova, H. Y. Hitkova, A. D. Bachvarova-Nedelcheva, R. S. Iordanova, N. K. Ivanova, M.P. Sredkova, *J. Univ. Chem. Techn. Metall.*, **48**(2), 154 (2013).
18. K. Marinaga, Y. Suginohara, Y. Yanagase, *J. Jpn, Inst. Met.*, **40**, 775 (1976).
19. S. Srivastava, R. Sinha, D. Roy, *Aquatic Toxicology*, **66**, 319 (2004).
20. W.-X. Liu, J. Ma, X.-G. Qu, W.-B. Cao, *Res. Chem. Intermed.*, **35**, 321 (2009).

СИНТЕЗ И ФОТОКАТАЛИТИЧНА АКТИВНОСТ НА Fe (III), N КО-ДОТИРАНИ TiO_2 НАНОЧАСТИЦИ

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(Резюме)

Дотирани с Fe(III) и N-TiO_2-наночастици са синтезирани при ниска температура по нехидролитичен зол-гел метод. Настоящата работа е продължение на нашите изследвания върху синтеза на наноразмерни TiO_2 прахове с подобрена фотокаталитична активност. Структурата и морфологията на получените проби е характеризирана с помощта на РФА, ИЧ и УВ-Вис спектроскопия. Дотирането с Fe и N не повлиява върху размера на частиците. Фотокаталитичната активност на дотираните прахове TiO_2 е изследвана в присъствие на УВ и видима светлина при фотодеградацията на Malachite Green като моделен замърсител. Посочена е зависимостта между концентрацията на допанта и фотокаталитичната активност.