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STSM SCIENTIFIC REPORT

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STSM Topic: Studies on photocatalytic properties of antiseptic TiO_2 layers (nanotubes and nanowires)

Host: Lars Pleth Nielsen, Tribology Centre, Danish Technological Institute, Aarhus (DK), lpn@teknologisk.dk

Carrying out the studies on photocatalytic properties of TiO_2 layers (nanotubes and nanowires) was the main purpose of the STSM, which has been held between 1st June and 14th June 2014, at Tribology Centre, Danish Technological Institute, Aarhus (Denmark). An additional purpose of the visit was to become familiar with PVD (Physical Vapor Deposition) method of TiO_2 thin films deposition, as well as taking part in the 16th Nordic Symposium on Tribology NORDTRIB 2014, which was held in Aarhus on 10-13 June 2014 and organized by Danish Technological Institute.

During a two-week stay at the DTI Tribology Centre in Aarhus, the following work has been carried out:
- deposition of titanium dioxide layers of three different thicknesses: 400nm, 800nm, 1200nm, using PVD technique. The depositions were carried out on an industrial scale CC800/9 SinOx coating unit from CemeCon AG in Germany;
- studies of photocatalytic properties of TiO_2 thin films deposited during the stay (by PVD), as well as TiO_2 layers (nanotubes and nanowires) brought to Tribology Centre from the home institution. These studies were based on the decomposition process of acetone to CO_2, by TiO_2 thin films induced by UV light and were carried out with the use of home-build set up; the scheme of the set-up is presented on Fig.1.

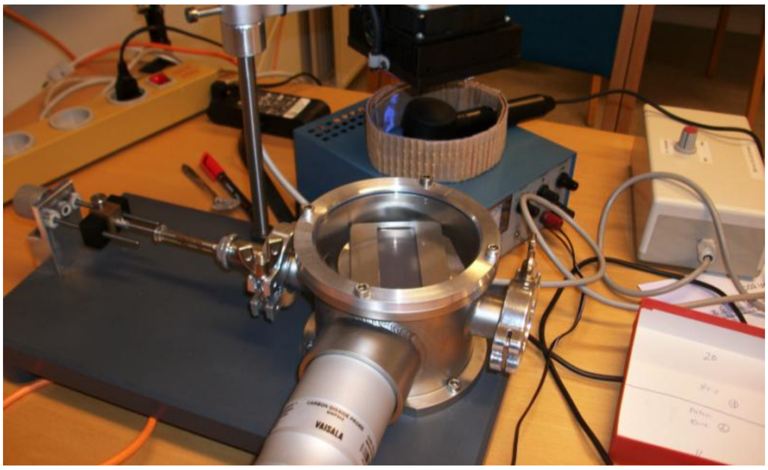


Fig.1. Set-up used to study the photodegradation of acetone to CO_2 in the presence of TiO_2 sample and UV illumination

- wettability measurements of TiO_2 thin films deposited by PVD, as well as TiO_2 nanotubes and nanowires. These measurements were carried out with the use of Krűss contact angle measurement system The morphology of the samples of TiO_2 deposited by PVD is shown on the Fig.2. According to data obtained from the members of Lars Pleth Nielsen research group, during the applied conditions of PVD processes, it is possible to obtain the anatase form of TiO_2

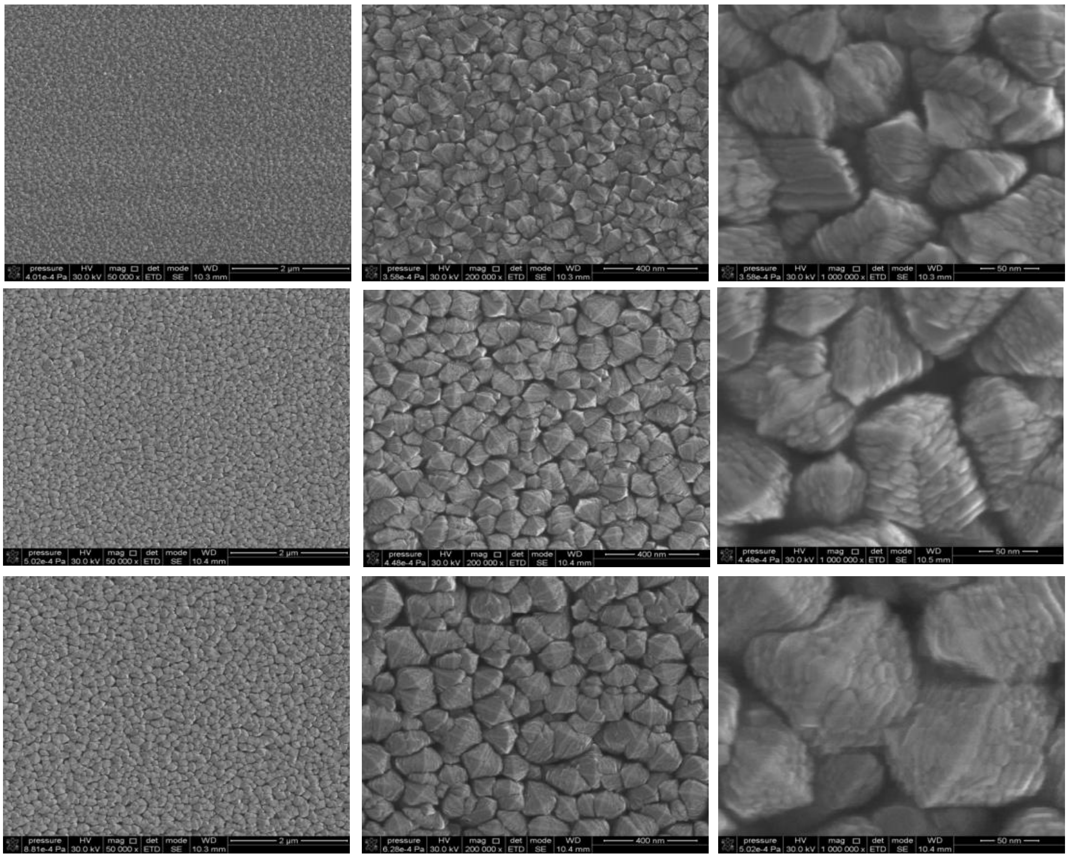
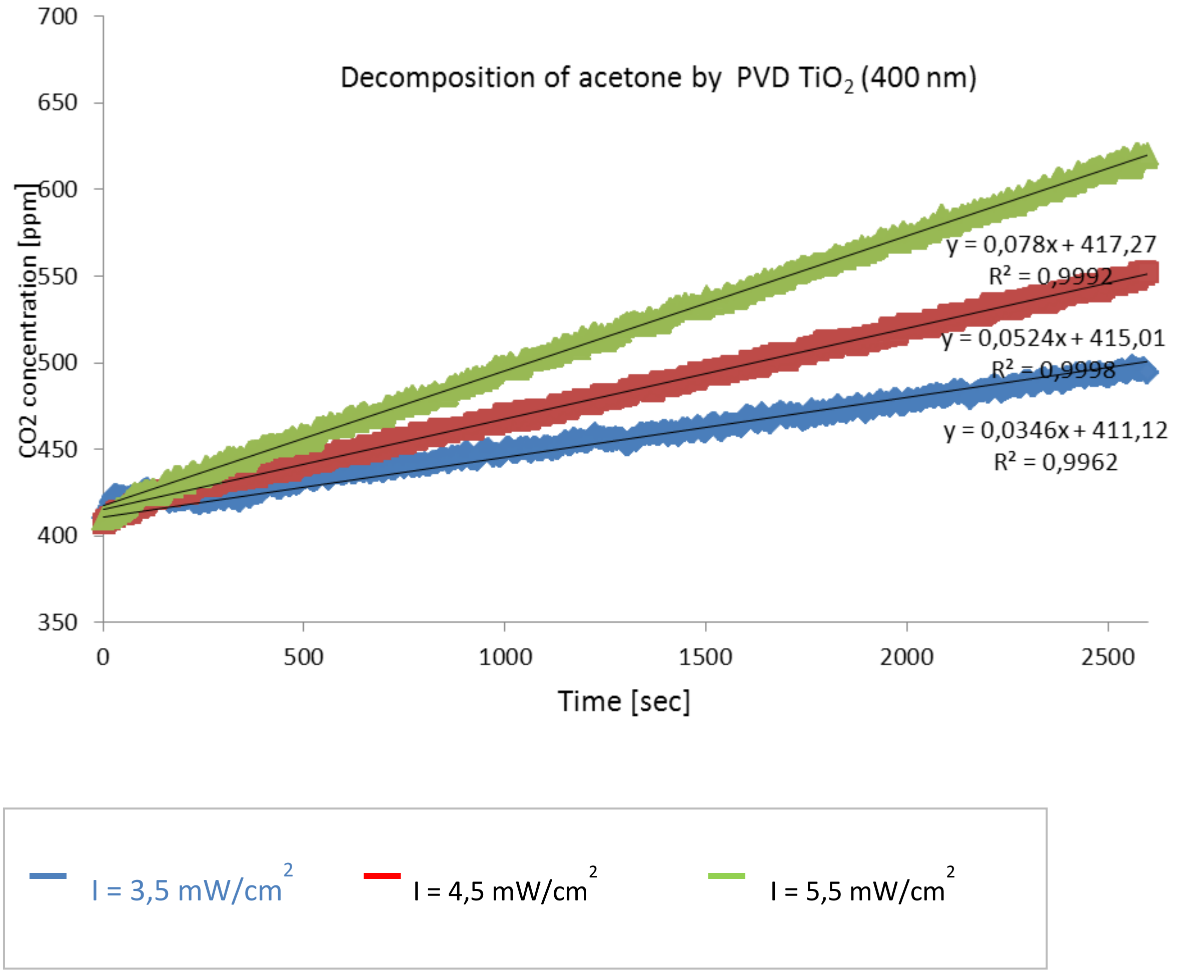
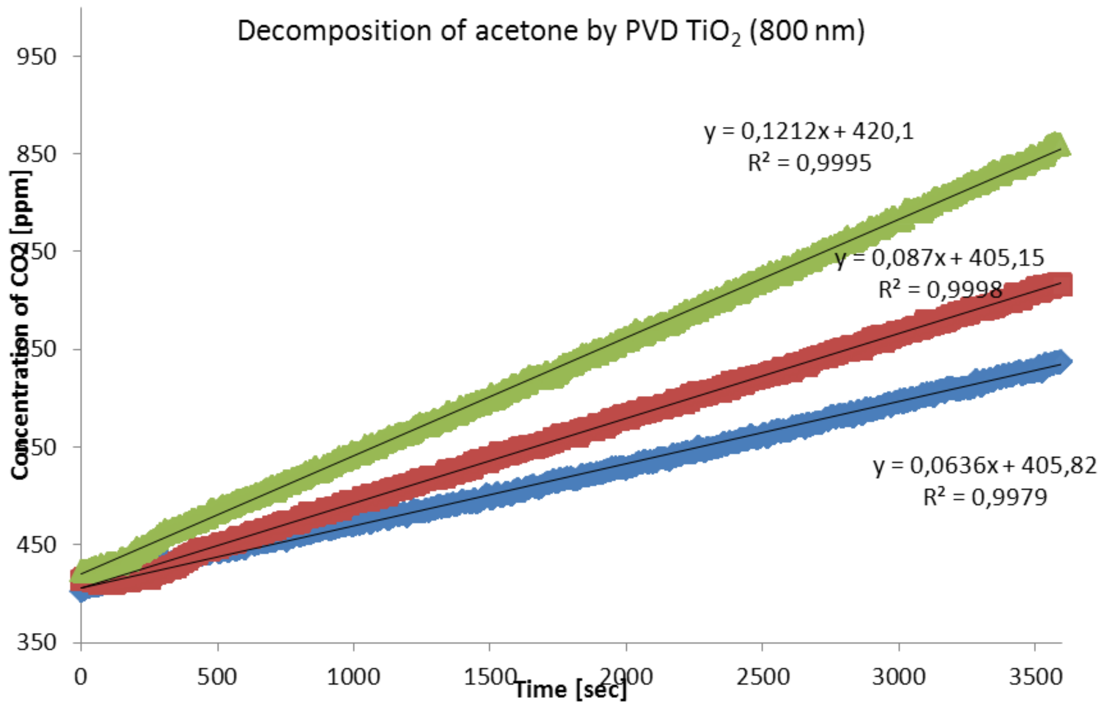
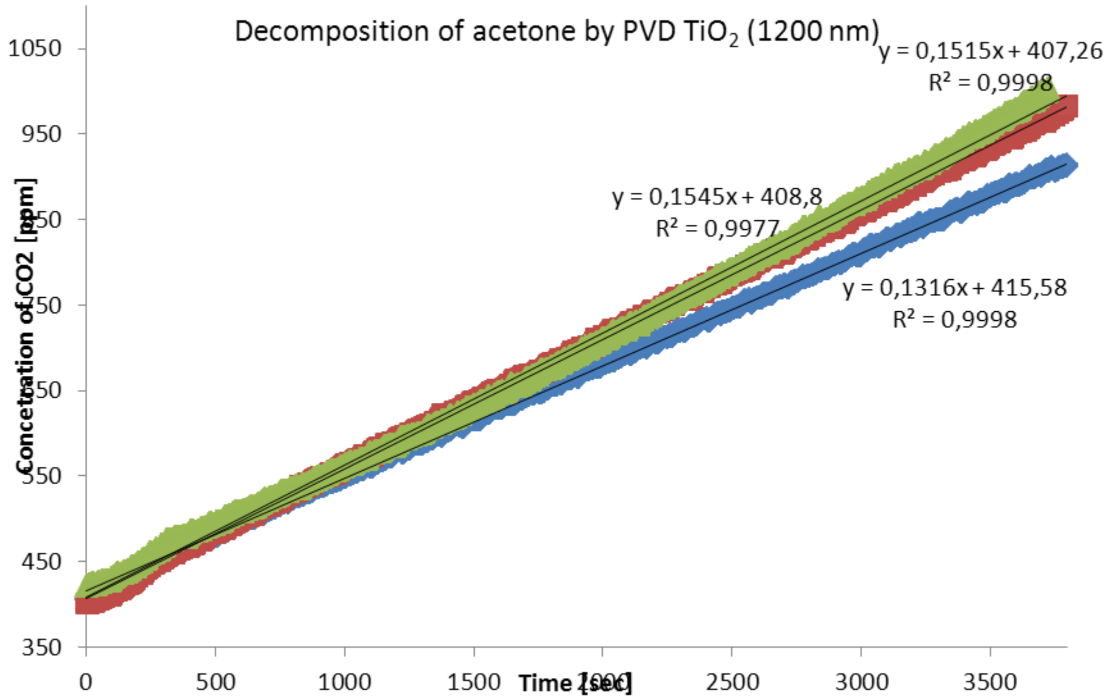


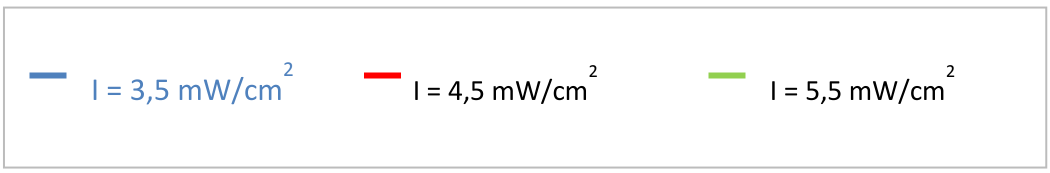
Fig. 2 SEM images of TiO_2 PVD of thickness: (a) – 400nm, (b) – 800 nm, (c) – 1200 nm

Graphs presenting the process of decomposition of acetone under the influence of UV light-induced layer of PVD TiO_2, are presented below:

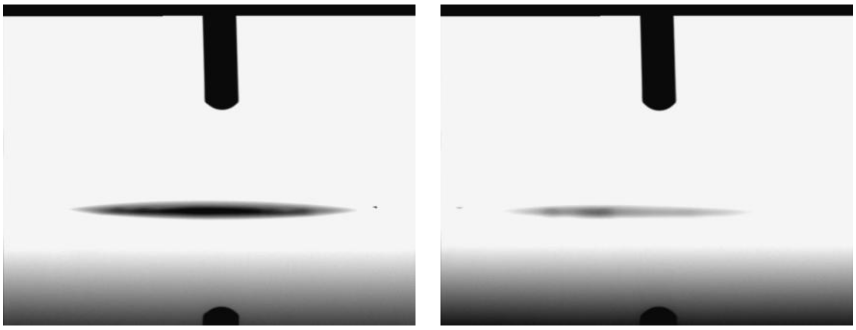



Decomposition of acetone by PVD TiO2 (800 nm)
y = 0,1212x + 420,1
R² = 0,9995
y = 0,087x + 405,15
R² = 0,9998
y = 0,0636x + 405,82
R² = 0,9979
Concentration of CO2 [ppm]
Time [sec]
950
850
450
350
0
500
1000
1500
2000
2500
3000
3500

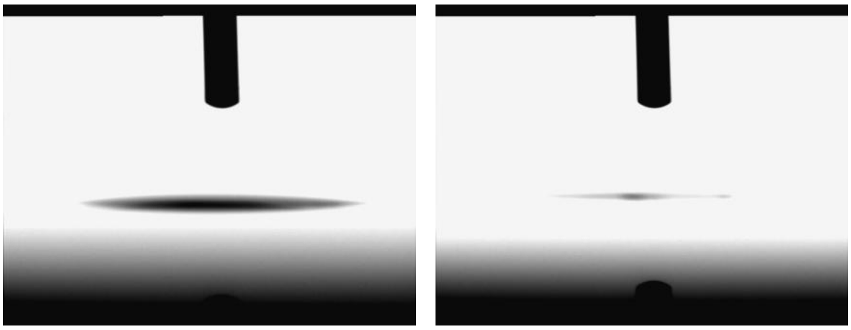

Decomposition of acetone by PVD TiO2 (1200 nm)
y = 0,1515x + 407,26
R² = 0,9998
y = 0,1545x + 408,8
R² = 0,9977
y = 0,1316x + 415,58
R² = 0,9998
Concetration of CO2 [ppm]
Time [sec]
1050
950
550
450
350
0
500
1000
1500
2500
3000
3500


I = 3,5 mW/cm2
I = 4,5 mW/cm2
I = 5,5 mW/cm2

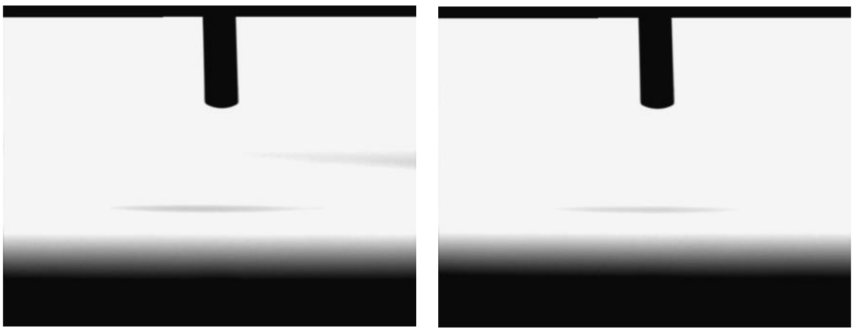
As photocatalytic activity is closely related to the superhydrophilic properties, the same samples were tested using Krűss contact angle measurement system. These studies proved the higher superhydrophilic properties of PVD TiO_2 layers. A few images recorded during the studies are presented below:



PVD TiO_2 400 nm
a) without UV
b) after 5 min UV illum.



PVD TiO_2 800 nm
a) without UV
b) after 5 min UV illum.



PVD TiO_2 1200 nm
a) without UV
b) after 5 min UV illum.

The titanium dioxide nanotubes on the titanium surface were fabricated, at home institution, by anodic oxidation. It is an electro-chemical process that changes the surface chemistry of the metal, via oxidation, to produce an anodic oxide layer. During this process a self organized, highly ordered layer of titania nanotubes were produced, with controllable pore diameters, length, wall thickness and periodicity. It is possible to obtain it by changing the value of voltage, time of anodization and using different types and concentration of electrolytes. This method involves the use of a titanium foil (99,98%) with a thickness of less than 0,5 mm as substrates (titanium foil play a role a material, which dental implants are made from). A titanium substrates was used as the anode and a platinum (Pt) sheet was used as the cathode submersed in a fluoride-based electrolyte solution (Fig.3.). The duration and magnitude of power supplied to the system determined the height and diameter of the nanotubes.

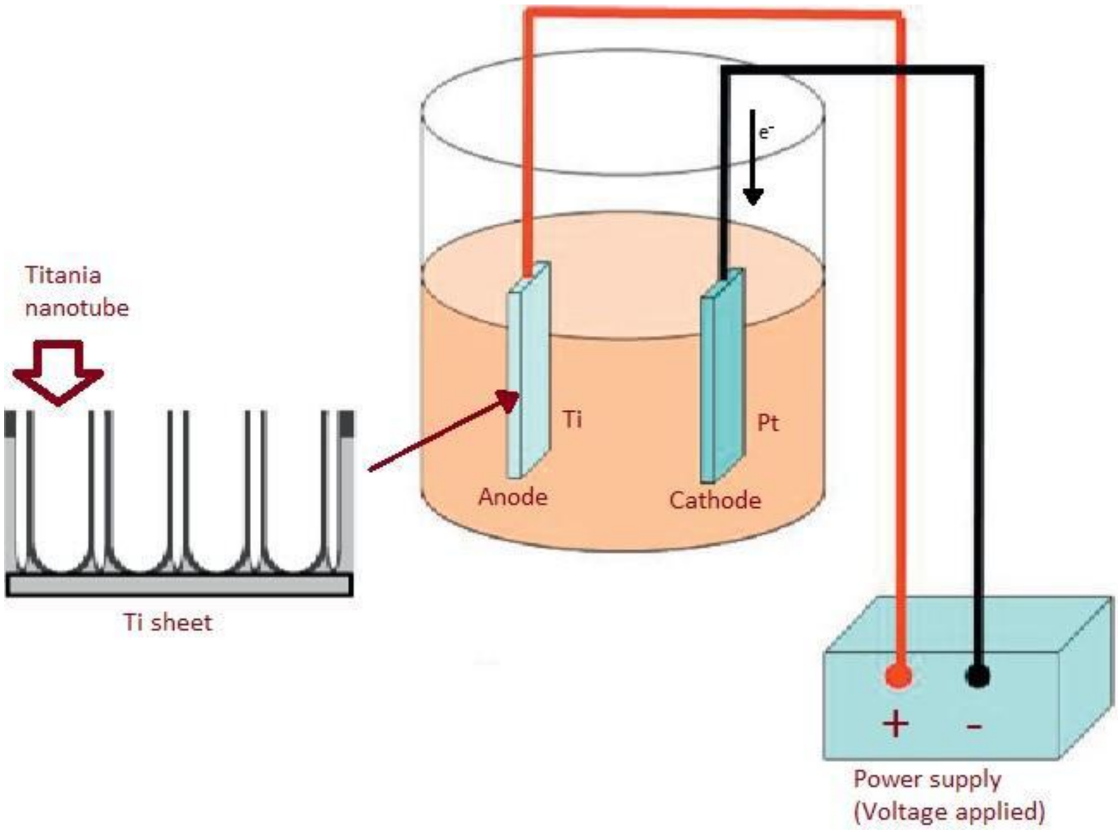


Fig. 3. A scheme of the TiO_2 nanotubes fabrication

Below there are SEM images of TiO_2 nanotubes, obtained by different value of voltage, presented.

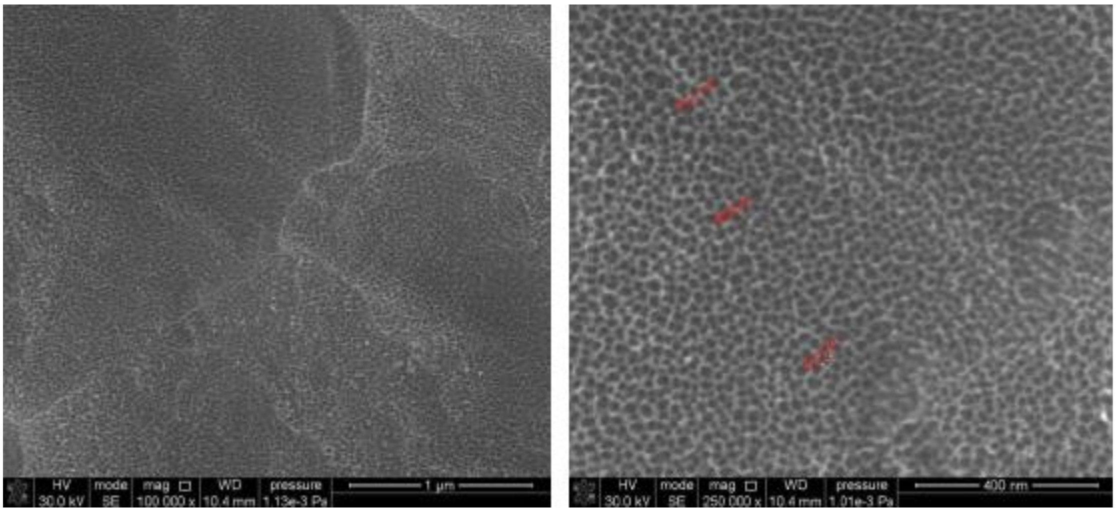


Fig. 4. SEM image of TiO_2 nanotubes fabricated at 3V

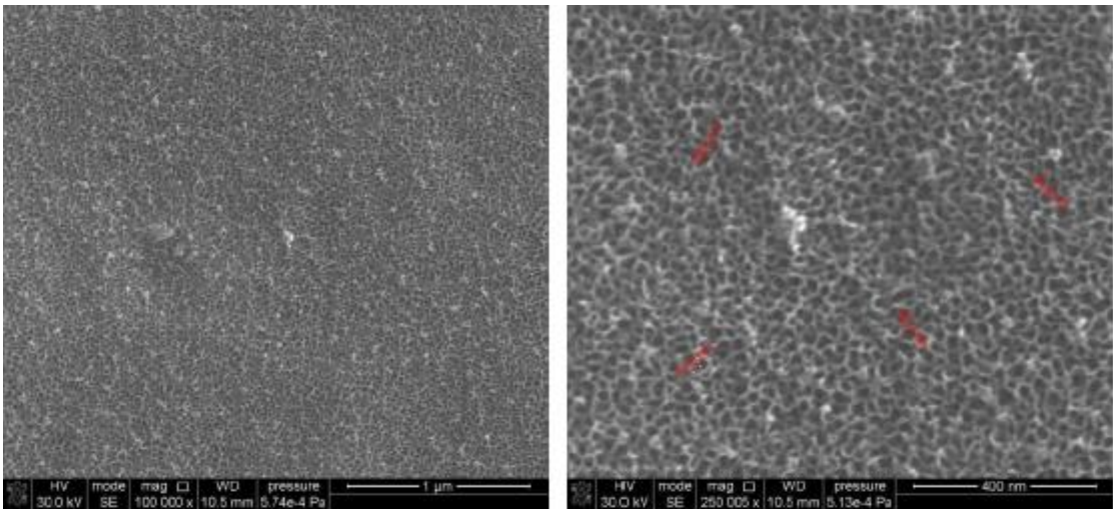


Fig. 5. SEM image of TiO_2 nanotubes fabricated at 4V

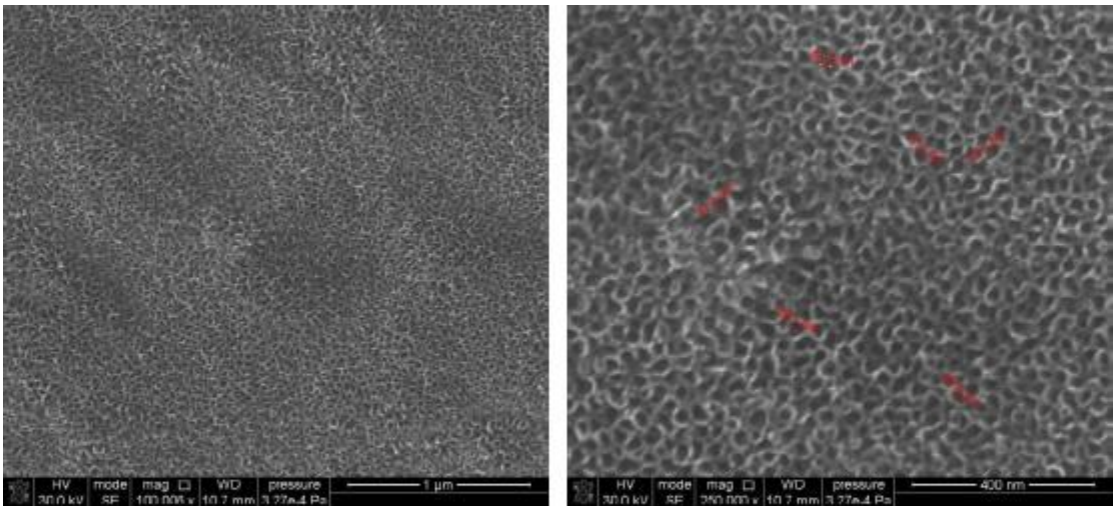


Fig. 7. SEM image of TiO_2 nanotubes fabricated at 6V

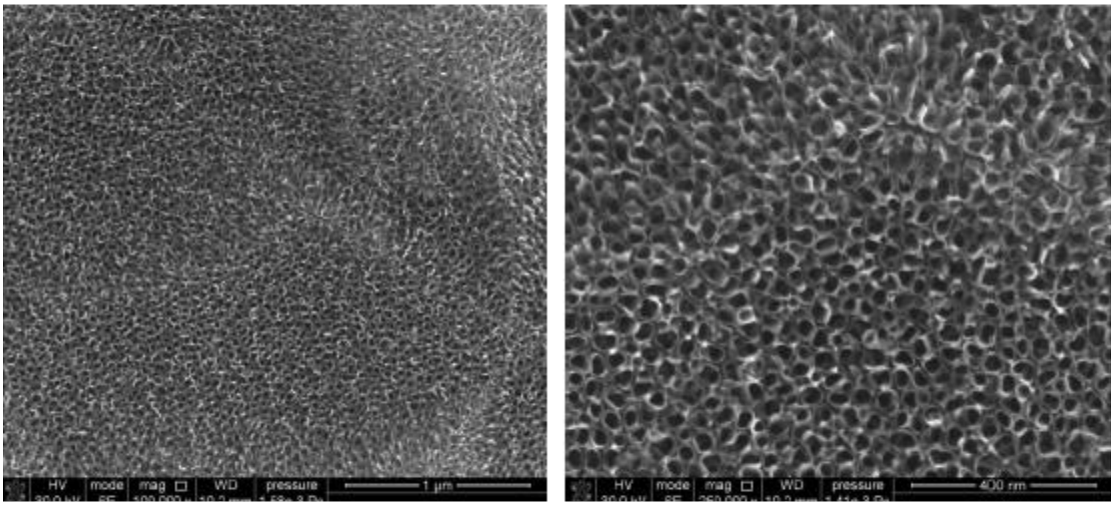


Fig. 8. SEM image of TiO_2 nanotubes fabricated at 8V

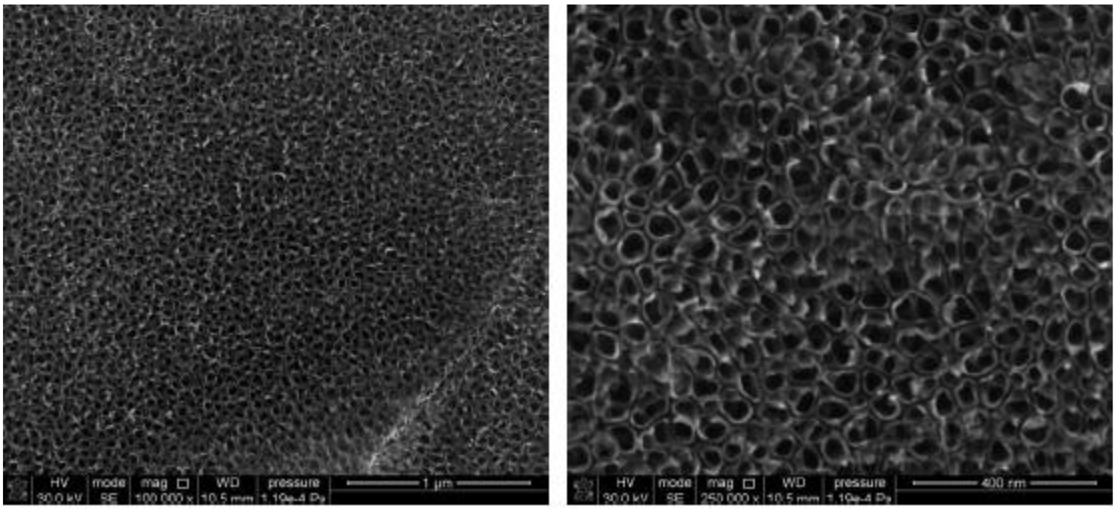


Fig. 9. SEM image of TiO_2 nanotubes fabricated at 10V

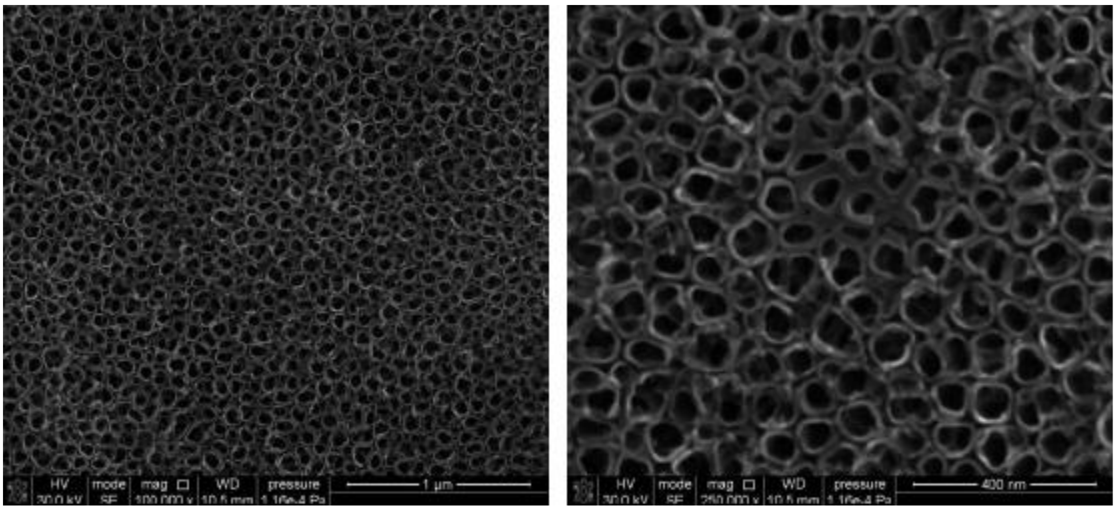


Fig. 10. SEM image of TiO_2 nanotubes fabricated at 15V

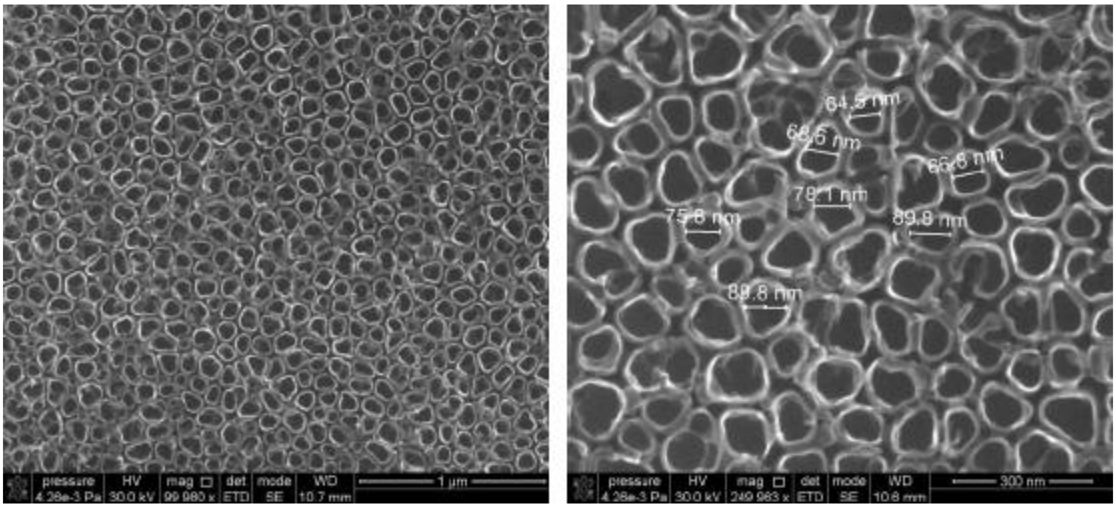


Fig. 11. SEM image of TiO_2 nanotubes fabricated at 20V

As it can be seen, the sizes of pores and the morphology of the nanotubes films differ for the different voltage applied. It can be obvious that the wettability and the photocatalytic activity should be also different for samples obtained in the range of voltage 3V-20V.

Below there are figures showing the activity of all samples illuminated by UV, in the process of decomposition of acetone into CO_2.

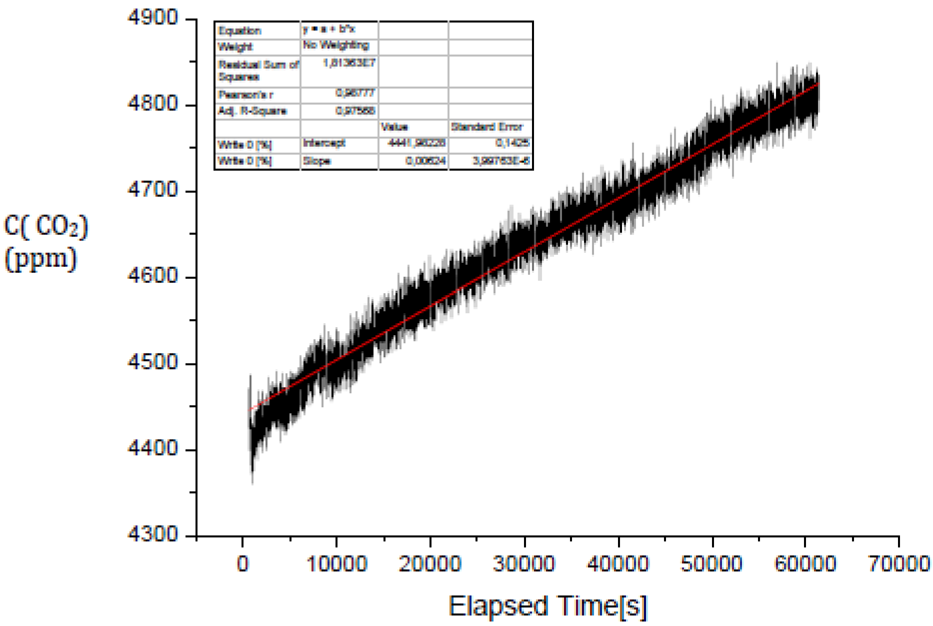


Fig. 12. Degradation of acetone by TiO_2 nanotubes obtained in the voltage of 3V

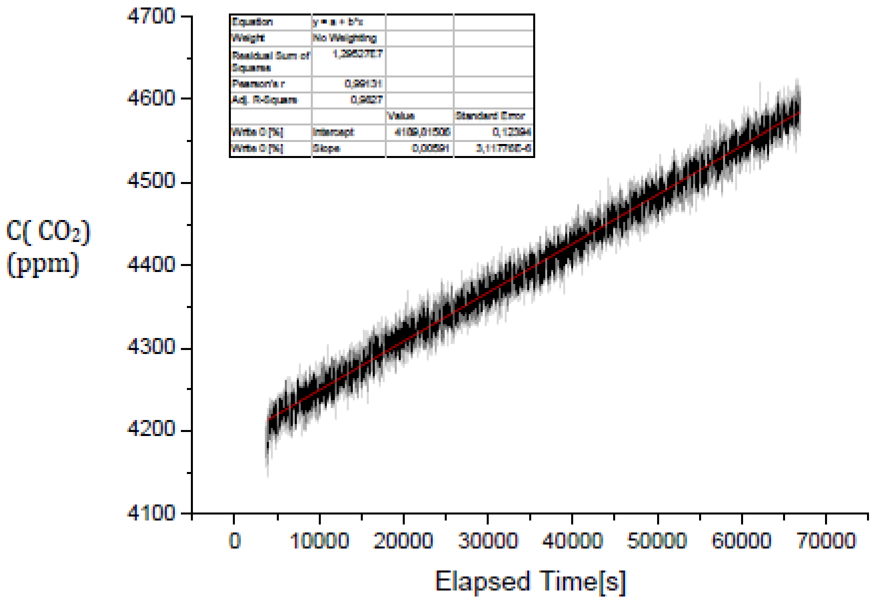


Fig. 13. Degradation of acetone by TiO_2 nanotubes obtained in the voltage of 4V

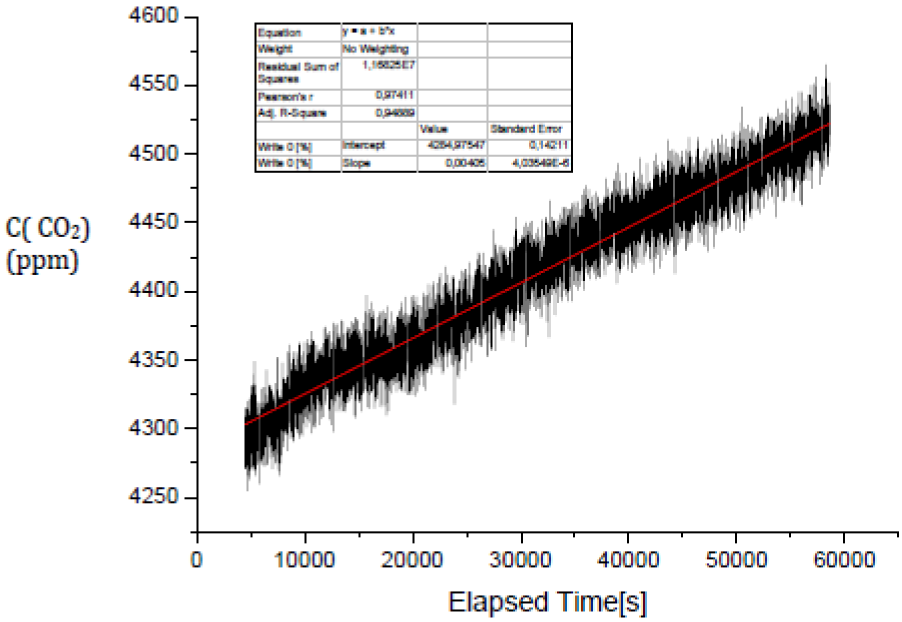


Fig. 14. Degradation of acetone by TiO_2 nanotubes obtained in the voltage of 6V

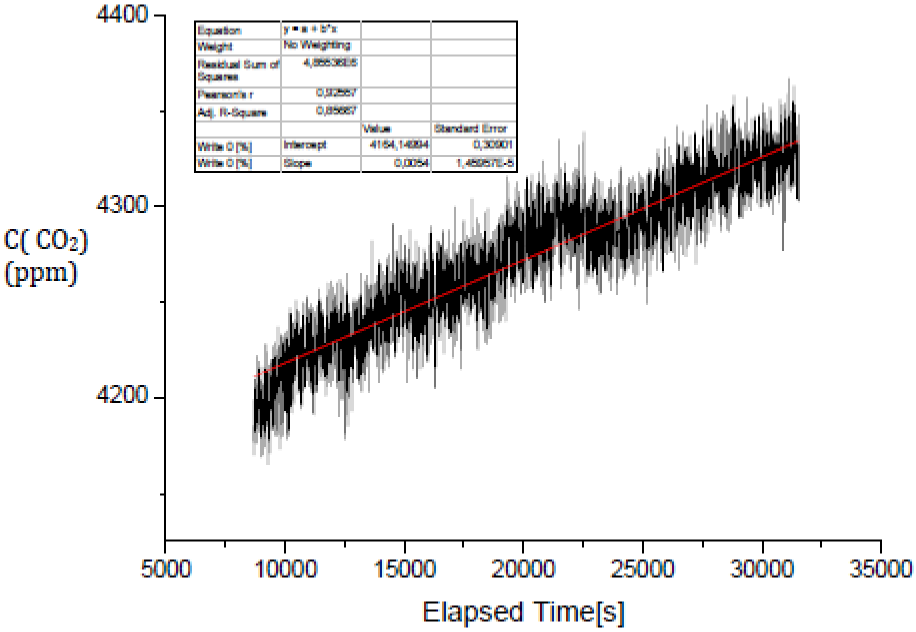


Fig. 15. Degradation of acetone by TiO_2 nanotubes obtained in the voltage of 8V

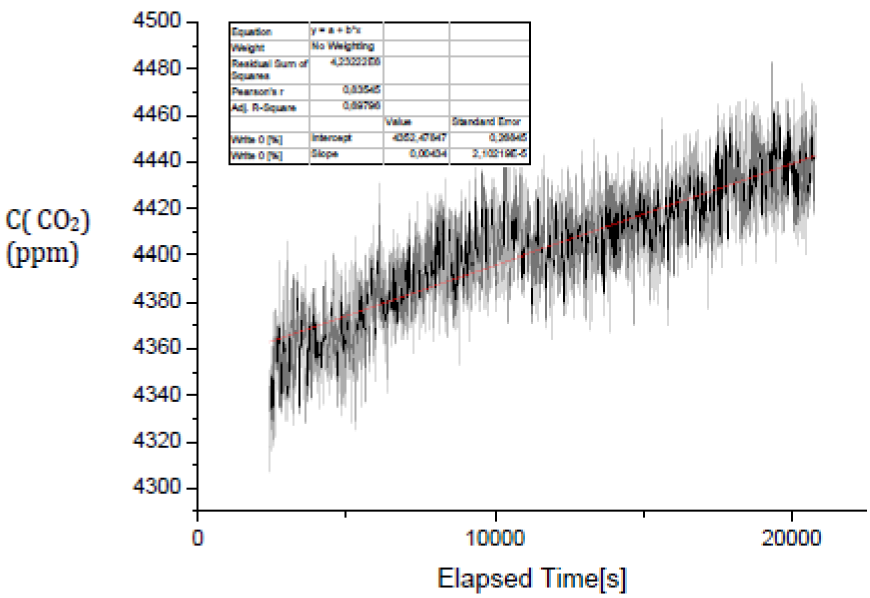


Fig. 16. Degradation of acetone by TiO_2 nanotubes obtained in the voltage of 10V

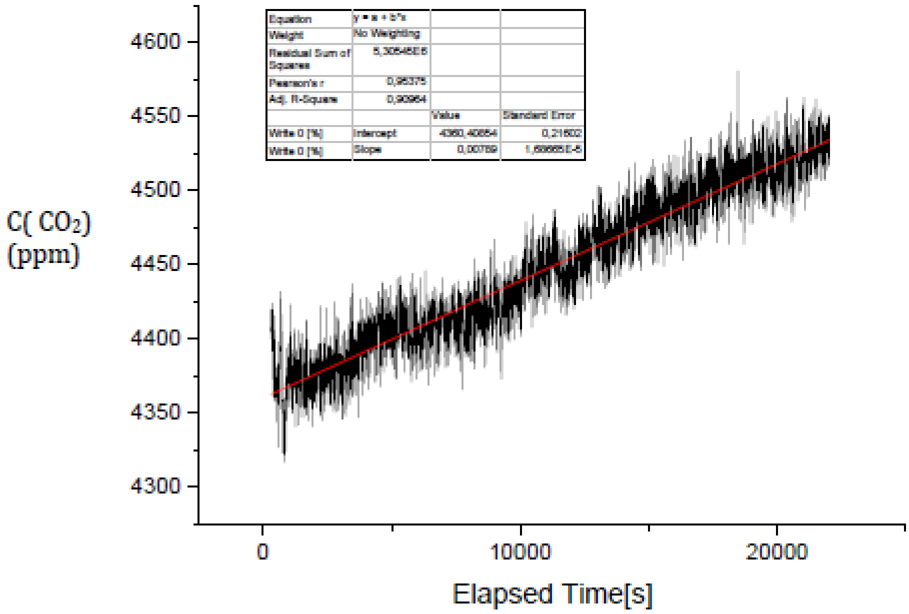


Fig. 17. Degradation of acetone by TiO_2 nanotubes obtained in the voltage of 15V

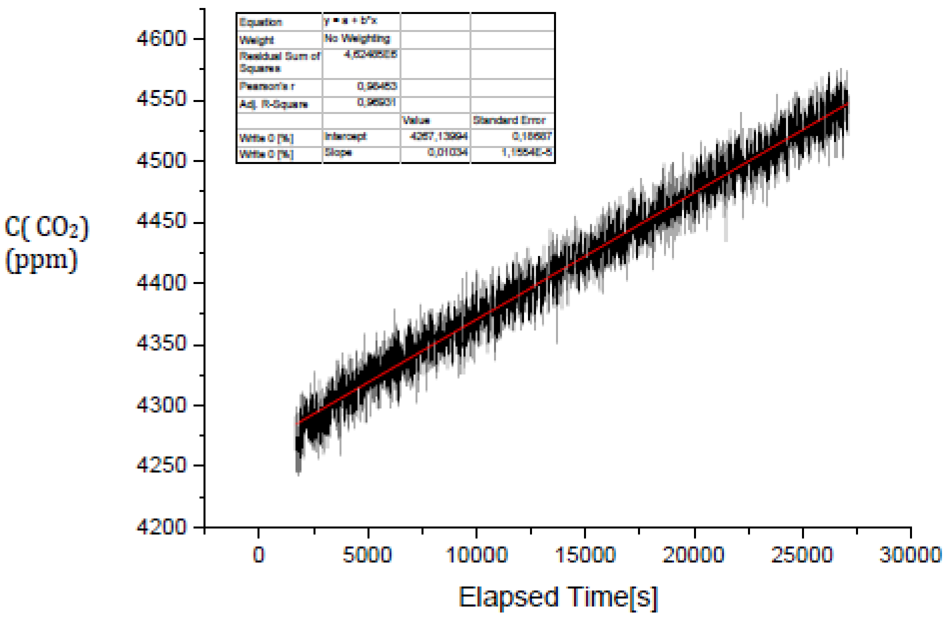


Fig. 18. Degradation of acetone by TiO_2 nanotubes obtained in the voltage of 20V

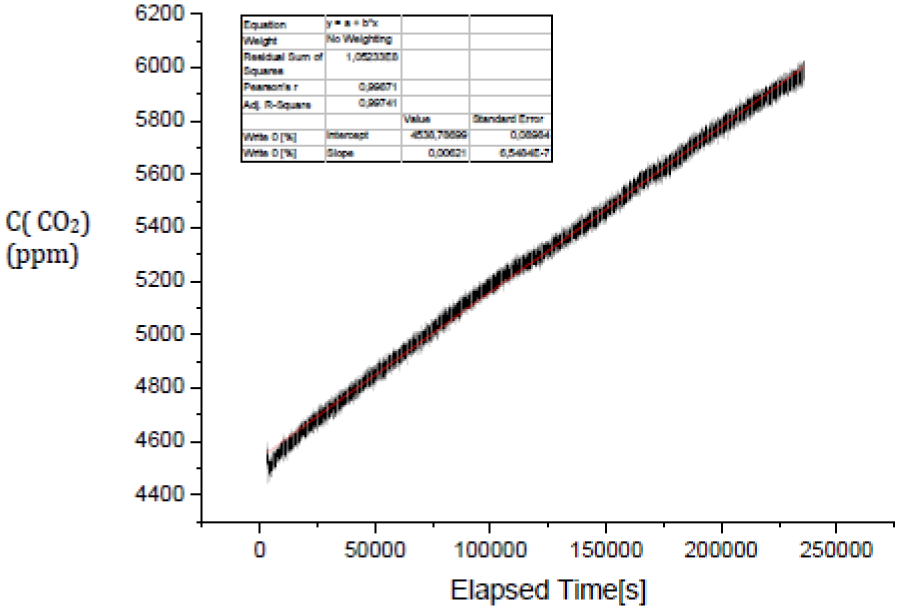


Fig. 19. Degradation of acetone by TiO_2 nanotubes obtained in the voltage of 20V – long term measurement

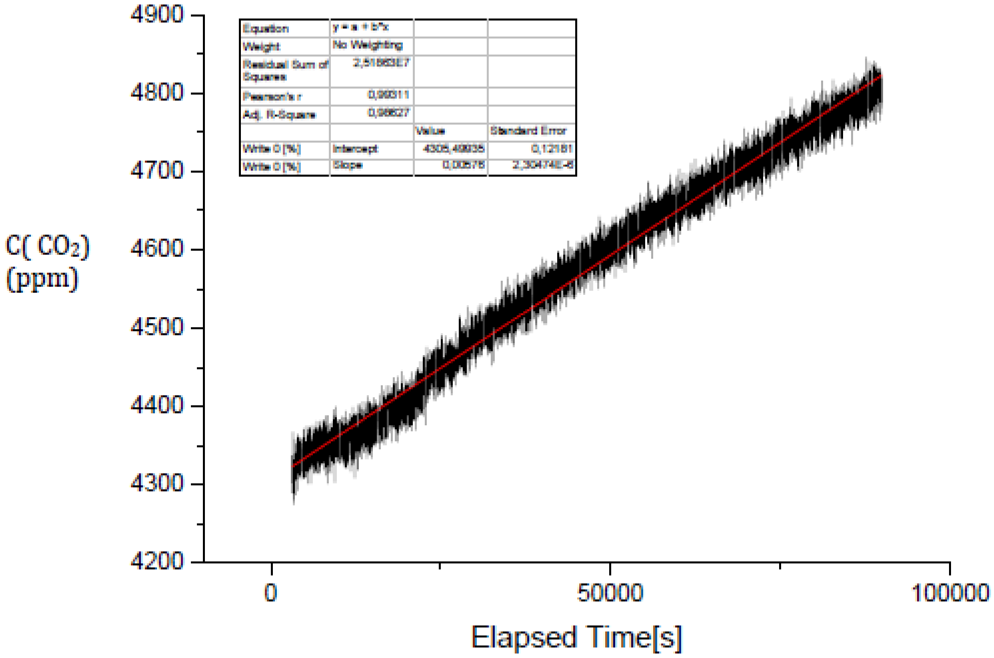


Fig. 20. Degradation of acetone by Pilkington Active glass sample

As it can be seen, the activity of TiO_2 nanotubes is dependent on the voltage used in their production. This fact is not surprising, as the morphology of the films of nanotubes and the size of pores is strictly dependent on the voltage used. As studied TiO_2 nanotubes are in amorphic form (in order to obtain anatase form of nanotubes, they should be annealed), the photocatalytic activity is not so high, as for example for anatase form. But it should be pointed out that their activity is comparable with Pilkington Active glass (Fig. 20).

The wettability studies of TiO_2 nanotubes were made without UV illumination and after 60 s and 120 s of UV illumination, of the intensity $I=4,5W/m^2$. The measurements were carried out with the use of Kruss contact angle measurement system. The results of studies are presented in the Table 1. The value of contact angle for every sample is the average value of ten measurements. Below Table 1, examples of photos made during the wettability studies of TiO_2 nanotubes are presented (Fig. 21 a-g)

Table 1. The results of wettability studies [°] for TiO_2 nanotubes

	Ti	TiO_2						
		3V	4V	6V	8V	10V	15V	20V
Without UV								
0 s	77,2±0,32	75,3±0,12	72,1±0,8	68,8±0,11	63,8±0,11	59,8±0,15	55,8±0,09	32,7±0,10
30 s	64,5±0,22	61,8±0,18	58,6±0,14	57,1±0,11	54,8±0,14	52,3±0,07	45,4±0,12	18,3±0,05
60 s	55,9±0,10	53,2±0,20	50,5±0,15	49,1±0,21	46,5±0,11	43,5±0,14	38,8±0,09	-
90 s	41,5±0,31	40,5±0,21	38,6±0,11	36,1±0,13	33,6±0,06	30,6±0,10	26,6±0,10	-
120 s	23,5±0,18	22,1±0,07	20,1±0,11	19,6±0,30	18,5±0,17	16,5±0,13	10,9±0,27	-
150 s	17,3±0,20	15,1±0,10	14,0±0,20	13,7±0,11	12,6±0,04	11,9±0,04	-	-
180 s	10,2±0,20	-	-	-	-	-	-	-
With UV (60s)								
0 s	76,0±0,11	31,1±0,07	27,1±0,17	25,1±0,06	21,1±0,01	17,1±0,11	15,1±0,17	-
30 s	62,2±0,42	27,0±0,06	21,2±0,17	19,6±0,12	17,9±0,32	14,1±0,11	-	-
60 s	52,3±0,13	21,3±0,12	17,6±0,22	15,3±0,14	13,2±0,20	-	-	-
90 s	39,8±0,29	14,0±0,11	10,2±0,10	-	-	-	-	-
With UV (120s)								
0 s	74,0±0,05	29,2±0,12	25,2±0,18	22,9±0,08	18,9±0,11	15,2±0,25	11,0±0,07	-
30 s	61,3±0,21	25,8±0,08	19,3±0,24	16,9±0,11	15,0±0,13	10,1±0,05	-	-
60 s	49,8±0,23	19,5±0,26	15,0±0,10	11,5±0,21	10,0±0,02	-	-	-
90 s	38,6±0,19	11,0±0,07	-	-	-	-	-	-

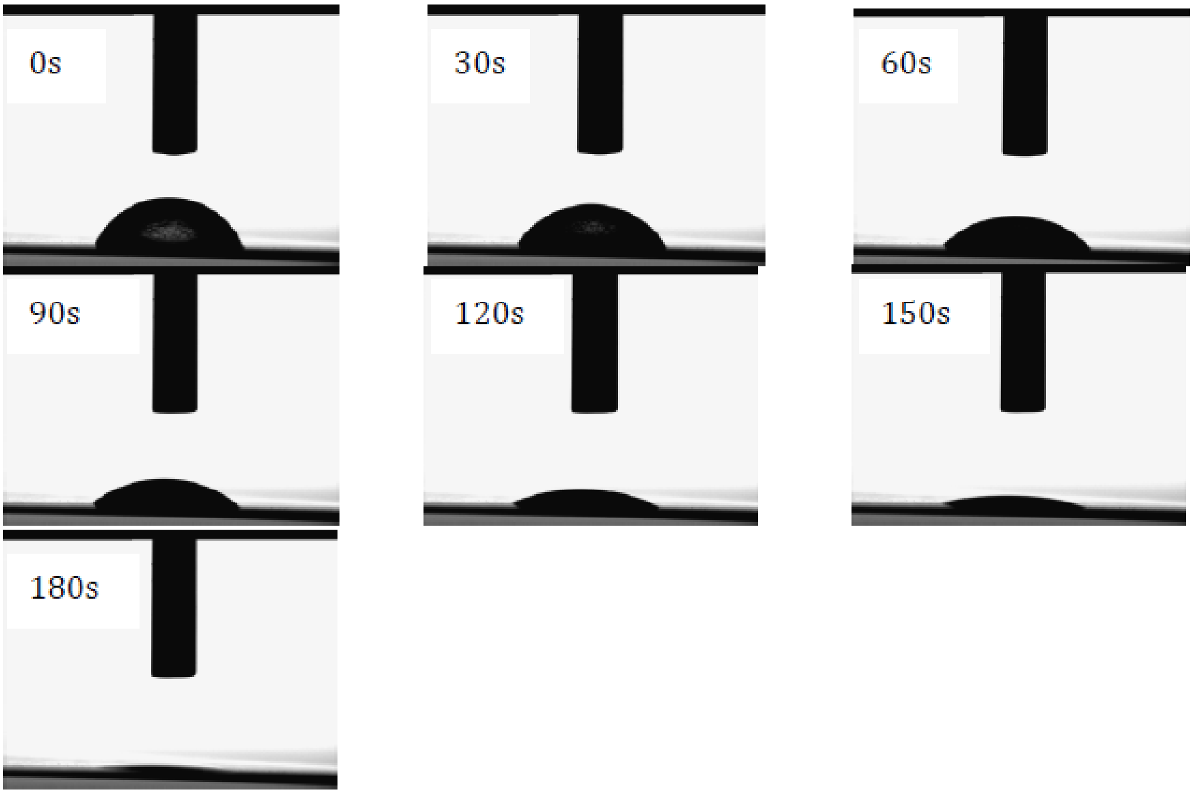


Fig. 21. Photos made during the wettability studies of TiO_2 nanotubes fabricated at 6V, without UV illumination.

Titania nanorods were obtained by the direct oxidation of titanium foil in the presence of the solutions consisted of: (a) H_2O_2 and HCl, (b) H_2O_2 and NaCl, (c) H_2O_2 and Na_2SO_4, (d) H_2O_2 and $CaCl_2$ and (e) only H_2O_2. SEM images of different titania nanowires morphology are presented below:

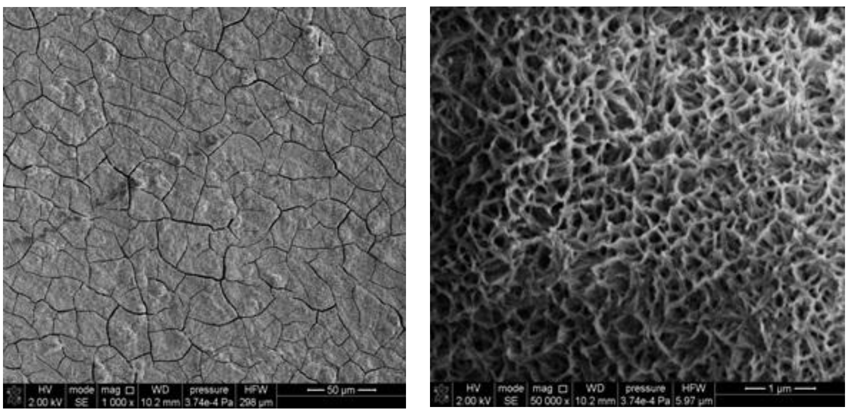


Fig. 22. SEM images of TiO_2 nanowires obtained with the use of H_2O_2 and HCl

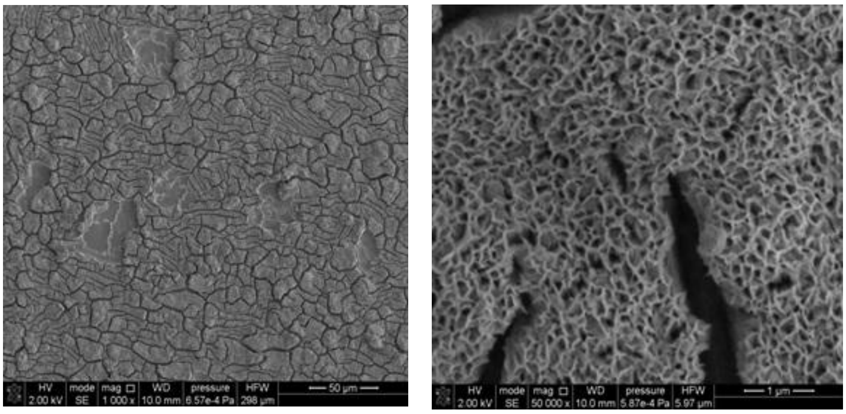


Fig. 22. SEM images of TiO_2 nanowires obtained with the use of H_2O_2 and NaCl

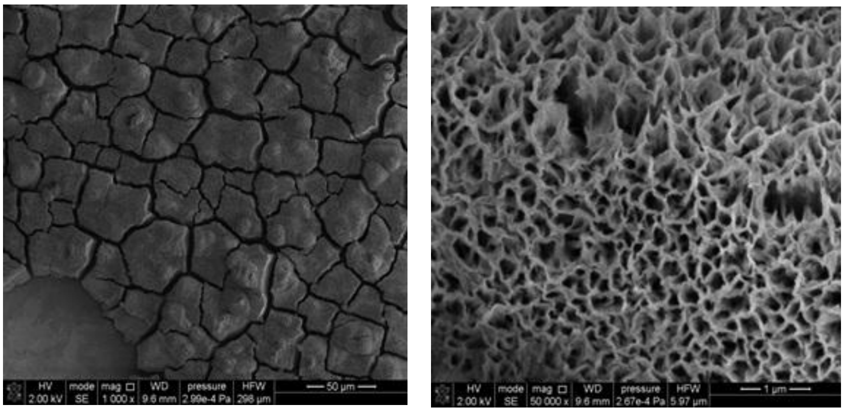


Fig. 23. SEM images of TiO_2 nanowires obtained with the use of H_2O_2 and Na_2SO_4

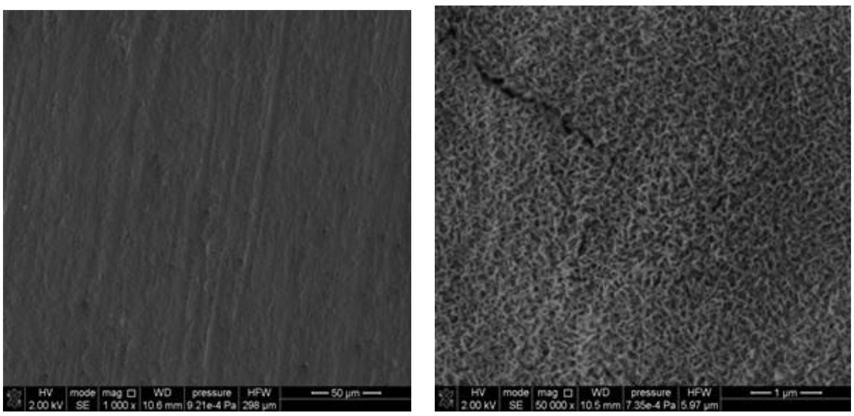


Fig. 24. SEM images of TiO_2 nanowires obtained with the use of H_2O_2 and $CaCl_2$

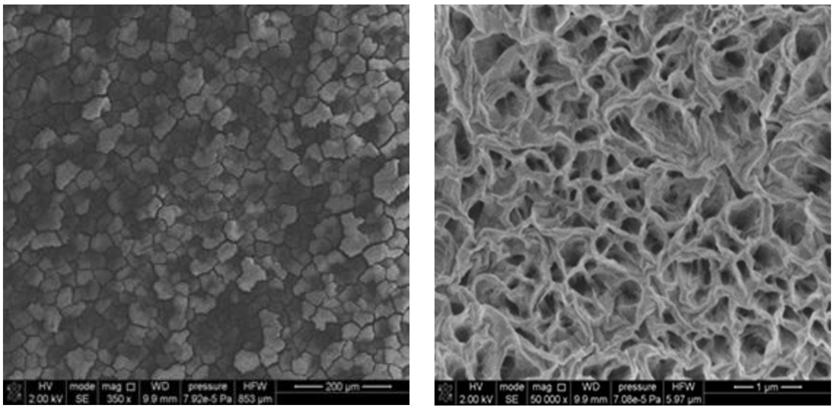


Fig. 25. SEM images of TiO_2 nanowires obtained with the use of H_2O_2

All the samples are amorphic but with the crystalline anatase islands, which was confirmed by DRIFT IR studies.

Below there are figures showing the activity of samples of titania nanowires illuminated by UV, in the process of decomposition of acetone into CO_2.

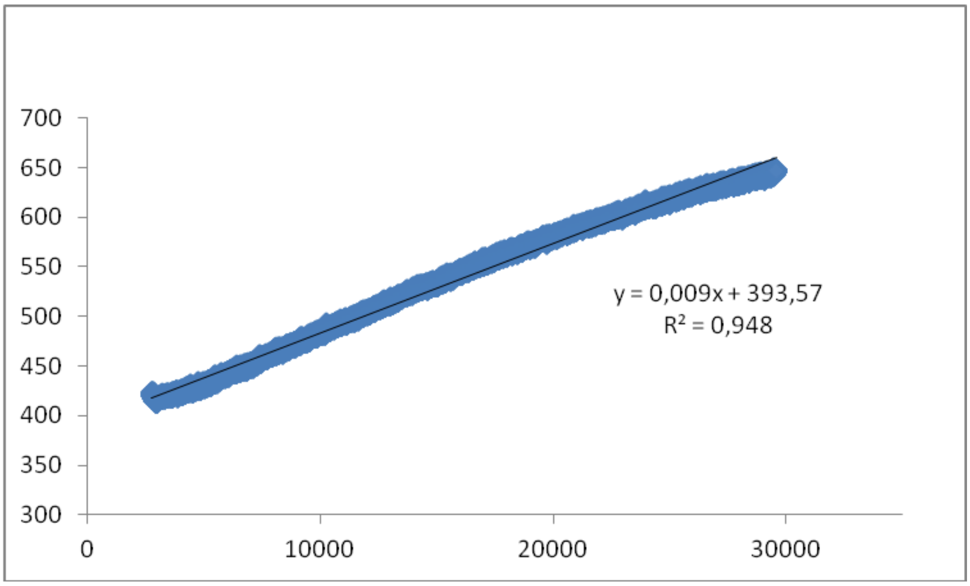


Fig. 26. Degradation of acetone by TiO_2 nanowires obtained with the use of H_2O_2 and HCl

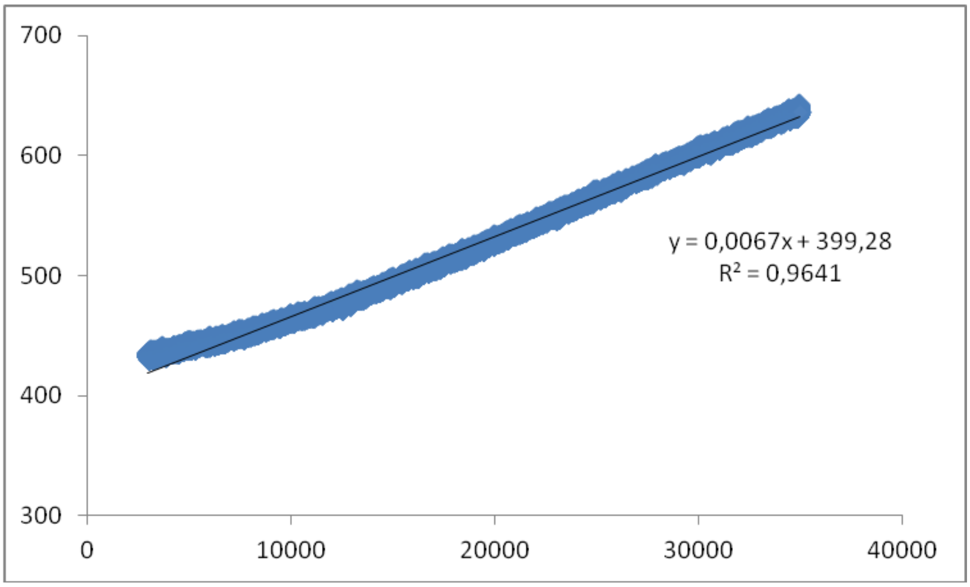


Fig. 27. Degradation of acetone by TiO_2 nanowires obtained with the use of H_2O_2 and NaCl

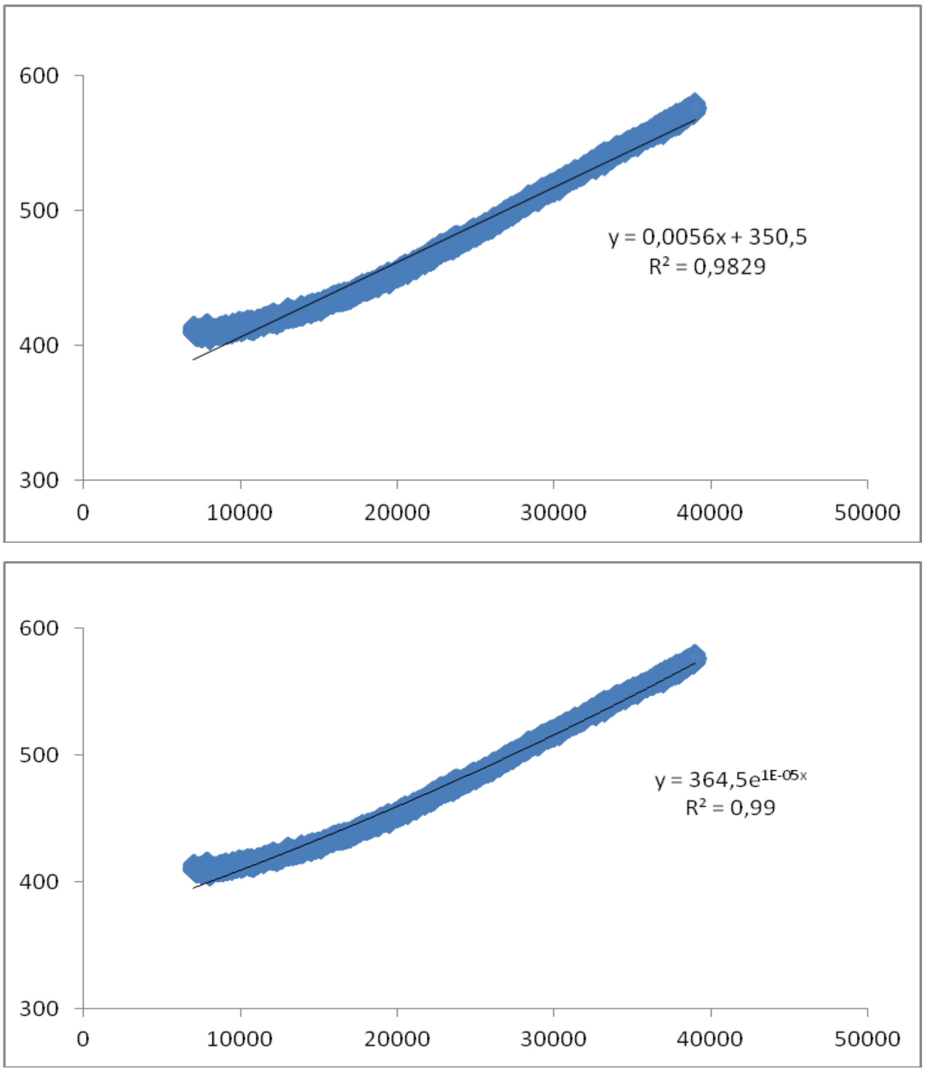


Fig. 28. Degradation of acetone by TiO_2 nanowires obtained with the use of H_2O_2 and Na_2SO_4 (Two different ways of regression)

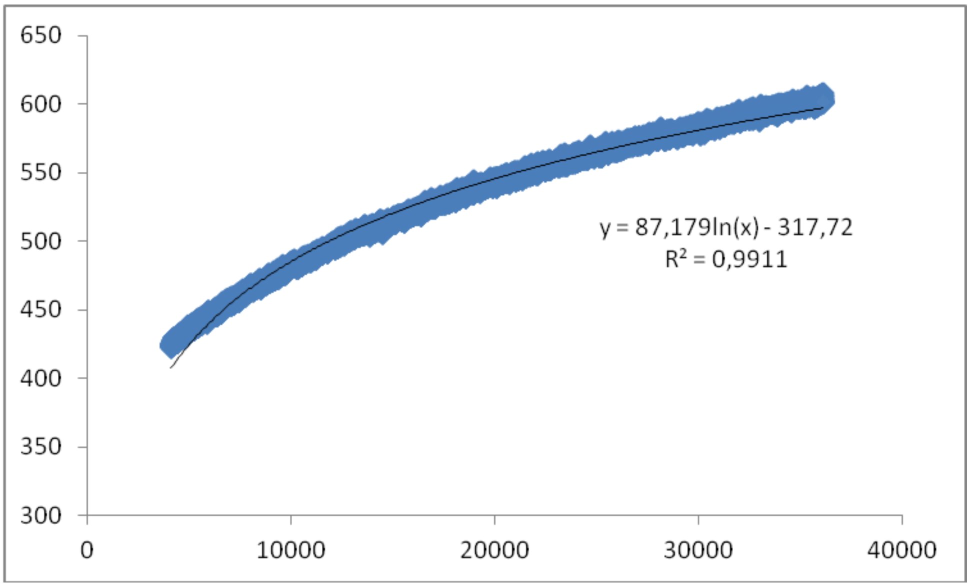
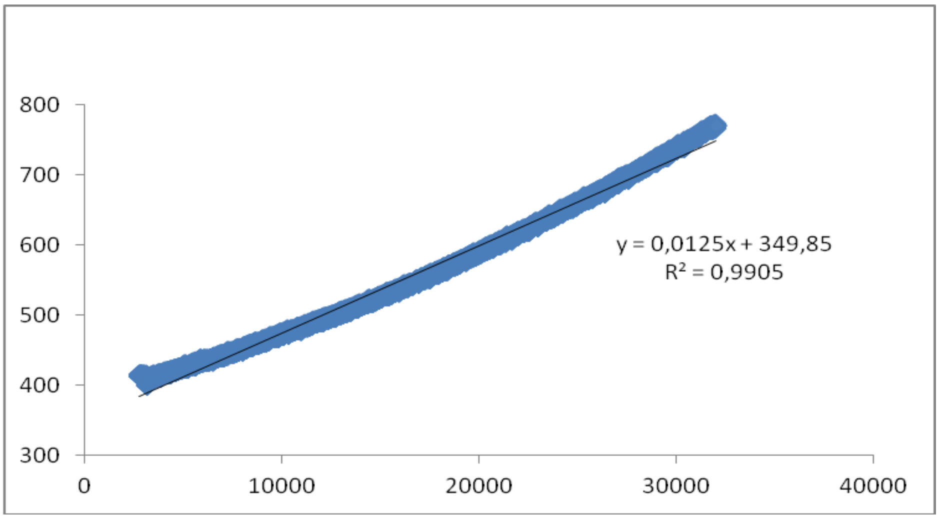


Fig. 29. Degradation of acetone by TiO_2 nanowires obtained with the use of H_2O_2 and $CaCl_2$



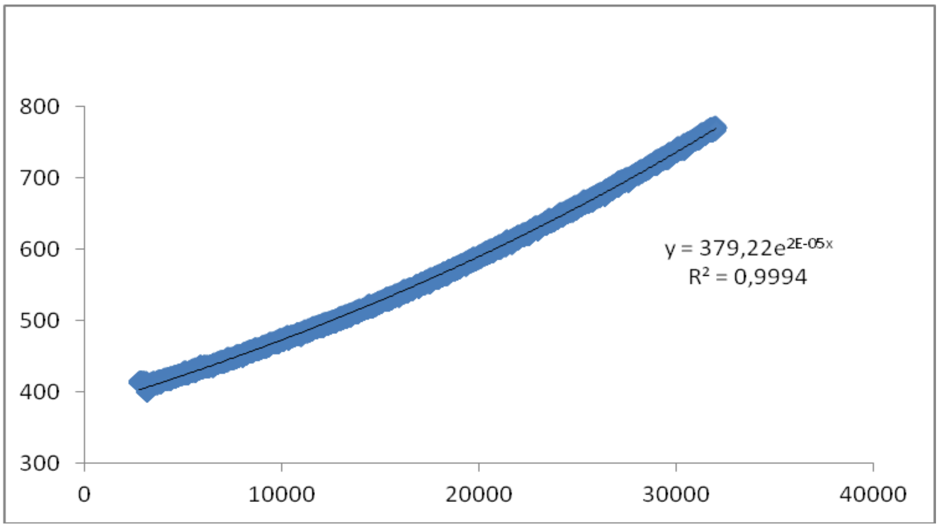


Fig. 30. Degradation of acetone by TiO_2 nanowires obtained with the use of H_2O_2

(Two different ways of regression)

The wettability studies of TiO_2 nanowires were made without UV illumination and after 60 s and 120 s of UV illumination, of the intensity I=4,5W/m^2. The measurements were carried out with the use of Krűss contact angle measurement system. The results of studies are presented in the Table 2. The value of contact angle for every sample is the average value of ten measurements.

Table 2. The results of wettability studies [°] for TiO_2 nanowires

	Ti	TiO_2 nanowires				
		H_2O_2+HCl	H_2O_2+NaCl	H_2O_2+Na_2SO_4	H_2O_2+$CaCl_2$	H_2O_2
Without UV						
0s	**77.2±0.32**	**55.1± 0.12**	**58.2± 0.16**	**58.8± 0.15**	**62.2± 0.12**	**33.0± 0.12**
30s	**65.4± 0.22**	**50.3± 0.10**	**51.3± 0.14**	**53.1± 0.05**	**55.0± 0.14**	**21.8± 0.14**
60s	**55.9± 0.10**	**42.2± 0.10**	**44.2± 0.06**	**48.2± 0.12**	**50.2± 0.11**	**14.5± 0.14**
90s	**41.5± 0.31**	**32.2± 0.09**	**35.2± 0.15**	**36.9± 0.12**	**38.7± 0.12**	-
120s	**23.5± 0.18**	**18.2± 0.15**	**20.3± 0.16**	**21.5± 0.08**	**22.2± 0.03**	-
150s	**17.3± 0.20**	**12.7± 0.14**	**14.8± 0.11**	**15.7± 0.12**	**16.2± 0.13**	-
180s	**10.2± 0.20**	-	-	-	-	-
With UV (60 s)						
0s	**76.0± 0.11**	**30.1±0.11**	**35.2 0.16**	**36.0 0.12**	**40.2 0.18**	**15.7±0.11**
30s	**62.2± 0.42**	**12.2±0.13**	**28.1 0.10**	**28.9 0.09**	**32.1 0.11**	-
60s	**52.3± 0.13**	-	**19.5 0.11**	**20.0 0.10**	**21.5 0.12**	-
90s	**39.8± 0.29**	-	-	**10.8 0.12**	**10.9 0.12**	-
With UV (120 s)						
0s	**74.0± 0.05**	**28.4±0.10**	**33.1 0.11**	**34.2 0.13**	**39.1 0.10**	**13.2±0.10**
30s	**61.3± 0.21**	**11.3±0.10**	**26.7 0.10**	**25.9 0.10**	**30.7 0.15**	-
60s	**49.8± 0.23**	-	**17.5 0.11**	**18.2 0.10**	**18.7 0.15**	-
90s	**38.6± 0.19**	-	-	-	-	-

The report presents only the data obtained during the STSM, without their deeper analysis. It is necessary to compare all the properties (photocatalytic properties and wettability) within the same group of coatings – nanotubes, nanowires - and also between them. Obtained results will be disseminated at coming conferences as well as published in peer review journals.