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Nanofibrous filtering materials with catalytic activity

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ABSTRACT

This research describes the fabrication of nanofibrous materials for the air purification with high filtration efficiency and catalytic properties to clean the air from solid particles and emissions of automobile's transport. The polyurethane (PU) nanofibers were modified by particles of SnO_2 and CrO_2 in the ratio 95/5 to impart catalytic properties in the reaction with emission gases (CO, NOx).The modification process was provided by the introduction of metal's oxide's particles of different concentrations (1;2; 3; 4%) into the polymer solution. Reological properties and conductivity of the modified solutions were studied. The viscosity of solutions grew up gradually with increasing of SnO_2/CrO_2 concentrations. Fiber's samples were produced from modified solutions by the electorstatic fiber forming using Nanospider technology. The morphology of produced fibers was analysed by the Scanning Electron Microscopy (SEM). SEM pictures confirmed the smoothness of fibrous layer. The diameters of fibres were measured with the help of Lucie 32G computer software. The obtained results demonstrated increasing of average diameters of nanofibers for the concentration 1and 2% of catalysts in comparison with the pure PU samples. But fibers with 3 and 4% of SnO_2/CrO_2 particles showed the decreasing of average fiber diameters. The presence of catalyst on the nanofiber`s surface was proved by the method of Energy Dispersive Spectroscopy (EDS). The catalytic properties of produced nanolayers in the reaction with emission's gases were studied with the measurement setup consisting from the engine, a system of analyzers and UV lamp as a sourse of energy to activate the catalyst. All samples demonstrated good catalytic efficiency. The best result showed the sample of PU nanofibers with 3% of SnO_2/CrO: the concentrations of CO and NOx reduced by 81% and 73% respectively. Produced samples are the promising materials for air-conditioning systems.

Keywords: Nanofibers; catalyst; air filtration; electrospinning.

Ganna Ungur received B.Sc. (Honours) and M.Sc. (Honours) degrees in Polymers and chemical fibers from Kiev National University of Technologies and Design, Kiev in Ukraine in 2009 and 2010 respectively. She is pursuing Ph.D. in the department of Nonwovens and Nanofibrous Materials of the Faculty of Textile Engineering, Technical University of Liberec, Czech Republic. Her field of research is nanofibers with catalytic activity for the purification of air from carbon monoxide and other emission's gases; modification of nanofibers with using of the individual metal oxides and their mixtures; preparation of nanofibres with antimicrobial activity; synthesis of composite catalysts for air purification to treat nanofiber filters.

Jakub Hrůza received his M.Sc. and Ph. D. degrees in Textile Engineering from Technical University of Liberec, Liberec (Czech Republic) in 1999 and 2006 respectively. Presently he is working as a Junior researcher in Institute for Nanomaterials, Advanced Technologies and Innovation at the Technical University of Liberec. His research activities have been focused in field of air and liquid filtration. He deals with the testing of filtration properties of the filter materials and the development of new filters with the using of nanofibers. Another area of his research activity is the processing of textile and polymer waste.

Introduction

Carbon monoxide as a toxic component of air has long been targeted for removal from air. Nowadays, air pollution by nitrogen oxides (NOx), mainly NO and NO_2, is also becoming an important environmental issue. Catalytic oxidation is the most effective means for its removal **[1]**. The scientific and engineering interest in the application of semiconductor photocatalysis has grown exponentially. Semiconductor photocatalysis with a primary focus on TiO_2 as a durable photocatalyst has been applied to a variety of problems of environmental interest in addition to

water and air purification **[2]**. Enhancements in photocatalytic activity over coupled semiconductors including CdS/TiO_2, ZnS/TiO_2, Cu_2O/TiO_2, and CuO/TiO_2, $WO_3/SiCeTiO$, $SrTiO_3/TiO_2$, SnO_2/TiO_2, Ta_2O_5/TiO_2, $CuO/Al_2O_3/TiO_2$ have been investigated extensively **[3]**.

Many oxides mainly act as a support material for dispersed metal catalysts. Tin oxide (SnO_2), however, is an oxidation catalyst in its own right. Tin-oxide based catalysts exhibit good activity towards CO/O_2 and CO/NO reactions. The activity and selectivity of SnO_2 catalysts can be substantially improved by incorporation of heteroelements. For instance the addition of copper, palladium, chromium and antimony increases the total oxidation of carbon monoxide and hydrocarbons **[4]**.

Many reports have been writen about using of SnO_2 as a gas sensor material. Gas sensor structure based on radio frequency sputtered SnO_2 thin film is found to be highly sensitive toward 10 ppm NO_2 gas, but with slow response and recovery times **[5]**. Synthesis of SnO_2 nanofibers functionalized by Pt nanoparticles with various loading contents (0.05–0.4 wt%) and their gas response toward H_2, NO_2, NH_3, CO, and SO_2 gases has reported. SnO_2-based gas sensorsfor detection of CO were investigated by doping Pt/SnO_2 nanoparticles with MoO_3, CeO_2, Sm_2O_3 and SiO_2 **[6-7]**.

But there is almost no information about the use of tin oxide as a photocatalyst material for the air purification from emission's gases in the literature. The photocatalytic oxidation of CO over NiO/SnO_2 photocatalyst has been investigated under UV irradiation. However, the influence of another additives (Cr, Cu, Sb) on the oxidative ability of SnO_2 remains unclear. Results showed that NiO/SnO_2 nanocomposites exhibits relatively high activity for oxidation of CO **[3]**. But such an approach solves the problem of air pollution from exhaust gases only partially, because nitrogen oxides are also harmful and undesired emission's components.

Another important reason of air pollution is a particulate matter (PM). PM is a general term used for a mixture of aerosol particles (solid and liquids) with a wide range in size and chemical composition. PM is either of natural origin or from anthropogenic sources, mainly from fuel combustion. Chronic exposure to particulate matter contributes to the risk of developing cardiovascular and respiratory diseases, as well as lung cancer. In addition to effects on the human health, PM can also have adverse effects on climate change and ecosystems **[8]**. Nanofiber filtration is drawing great interest nowadays because of its large surface collection area as well as low air resistance. The aerosol particle size-range between 100 and 500 nm is called the most penetrating particle size (MPPS). The results of the experiments confirmed that using nanofibrous filters a significant growth of filtration efficiency for the MPPS range can be achieved. During the past few decades, electrospinning technique has been paid a considerable attention due to production of fibers having diameter in the range of few microns to nanometer scale by applying high electric fields. Nanofibrous filtering media could be used for filtration of blood, water, air, beverages, gases, chemicals, oils, diesel and petrol, etc. **[9-10]**.

The objectives of this research were the production of polymer's nanofibers material with the high filtration activity, using an industrial electrospinning technique, and its modification to impart the catalytic properties in the reactions with CO and NOx. As a result, PU nanofibers, containing particles of two metallic oxides (SnO_2/CrO_2), have successfully produced by the Nanospider technique. Moreover, the structure and chemical composition of nanofiber matrices were investigated. Catalytic and filtration efficiencies have been evaluated. According to the obtained results, fabricated samples can find their application as a material for the air purification in the modern air-conditions systems.

The novelty of current study is in the combination of filtration properties of nanofibers and photocatalytic activity of SnO_2 promoting by CrO_2. The main advantage of fabricated fibrous composite materials is in its multifunctionality: air purification from solid particles and from emissions, which are harmful for human health and dangerous for the ecological situation.

Experimental

Materials

In this work, polyurethane (Larithane LS 1086, aliphatic elastomer based on 2000g/mol, linear polycarbonated diol, isophorone diisocyanate and extended isophorone diamine), was used as a polymer. The solution was prepared at 15 wt% concentration with dimethyl formamide (DMF) solvent. Tetraethylammoniumbromide was used as an additive to increase the conductivity of polyurethane solution. Polyurethane was obtained from Larithane Company, dimethylformamide and tetraethylamoniumbromide were purchased from Penta (Czech Republic) and Fluka (Netherlands). SnO_2 and CrO_2 powders (99.9% trace metals basis) were obtained from Sigma Aldrich Company (United Kingdom).

Solutions and their properties

Different concentrations (1; 2; 3 and 4%) of SnO_2/CrO_2 (in the ratio 95/5) were incorporated into the solution of polyurethane. Obtained systems were mixed on the magnetic stirrers for 48 hours. Rheological properties and conductivity were measured to understand the influence of used additives on the polymer solution. The viscosity was investigated using Rheometer HAAKE Roto Visco 1 at 23 °C. The electrospinning process fundamentally requires the transfer of electric charge from the electrode to the spinning droplet at the terminus of the tip **[11]**. A minimal electrical conductivity in the solution is therefore essential for electrospinning, that is why the conductivity of all solutions was determined by Eutech Instruments Con 150.

Electrospinning process

Roller spinning method (Nanospider) with high voltage power supply was used to produce nanofibers (**Fig. 1**). Nanospider is the unique method which has been used in industry to produce nanofibers continuously. Also this method is the first for all over the world, which was commercialized under the name of Nanospider from Elmarco Company in Liberec.

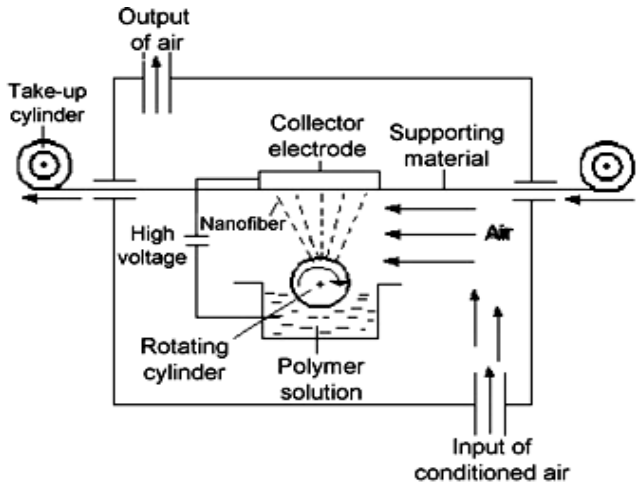

Fig. 1. Schematic diagram of Nanospider method.

Nanospider consists of rotating cylinder to spin fibers directly from the polymer solution. The PU polymer solution with particles was filled into a polypropylene dish and the bottom of aluminum rotating cylinder body with spikes was partially immersed into the polymer solution. High voltage is connected to the rotating roller. The collector electrode was usually grounded to create potential difference (**Fig. 1**). As the solvent evaporates, the jets of polymer solution were transformed and the solid nanofibers were obtained before reaching to the collector electrode. The nanofibers were collected on polypropylene (PP) spunbond nonwoven antistatic material.The solutions were electrospun at 65 kV with and 15 cm working distance (the distance between the spinning roller and the collector). Humidity (25%) and temperatures (20°C) inside of spinning chamber were controlled with the climate-control system.

Morfology of produced fibers

The fibers structure and diameters were determined by a scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM with EDS). The surface density of nanofibers layers with different concentrations of catalytic agents was calculated. Average diameters of fibers were measured from the SEM photos using Lucie 32G computer software. Fiber uniformity was determined using the number and weight average calculations. Number average has been known as an arithmetic mean in mathematics science. The method which was used to calculate the uniformity coefficient has the same principle with molar mass distribution in chemistry science. We calculated both of these values using the formulas 1 and 2 were given below:

$$A_n = \frac{\sum n_i d_i}{\sum n_i} \text{ (number average)} \quad (1)$$

$$A_w = \frac{\sum n_i d_i^2}{\sum n_i d_i} \text{ (weight average)} \quad (2)$$

where d_i is, fiber diameter and n_i is, fiber number. The fiber uniformity coefficient was determined by ratio A_w / A_n and optimum value should be much closed for 1 for uniform fibers **[12]**.

Test to determine the catalytic efficiency

There is no appropriate standardized methodology for the verification of catalytic function of nanofibrous layer. Our samples were wound on the porous body, which was placed into the filtration container. UV lamp for initiating of catalysts was installed inside of the porous body (**Fig. 2**).

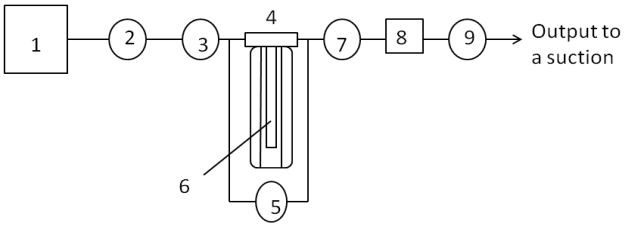

Fig. 2. Scheme of the measuring setup, where 1- the combustion engine; 2 – cooling of the emission's gases; 3 – valve of the sample collection before the filter; 4 – filtration container; 5 – differential pressure transmitter; 6 – UV lamp; 7 – valve of the sample collection after the filter; 8 – suction pump for the sample of exhaust gases; 9 – rotameter.

Aspirated inline three-cylinder combustion engine Skoda 1.2 HTP has chosen for the experiment as a source of emissions. The measurement set-up was equipped with an electric asynchronous dynamometer. So it was possible to adjust the operating conditions of the engine and maintain them stable for a long period. It means that the concentrations of exhaust gas components remain almost unchanged, because thermal steady operation mode is achieved. The observation of changes of pre-measured gaseous concentrations was done during their passage through the filter. Nitrogen oxides and carbon monoxide were main monitored components. Chemiluminescent and infrared analyzers were used to detect concentrations of NOx and CO respectively. These analyzers are commonly used for tests of combustion engines to determine the quantity of different gases in the exhaust sample. The test method number MP-04-95 was used to detect concentration of CO in exhaust gases of combustion engines by infrared analyzer Hartmann-Braun URAS 3E. Measuring effect is based on the absorption resonance of rotating absorption bands which is specific for individual heteroatom gases in the range of middle infrared spectrum between 2.5µm and 12µm of wavelength. In this range an oscillation of molecules lies, absorption of the radiation occurs with separate frequencies that are associated with self-oscillations of molecules. Individual gases are identified by their own absorption bands. A non-dispersed method is used to measure the absorption. There is no a spectral decomposition of infrared radiation in this method. The second using test method was MPAL 02/95 for the detection of NOx by chemiluminescent analyzer HORIBA CLA 150. The concentrations of monitored gases were measured before and after the filter. The measurement position (before or after the filter) was changed during the test by system of valves.

Measurement of the filtration efficiency

The filtration efficiency of PU nanofibers and nanofibers with catalysts was measured on the Sodium Chloride aerosol test equipment (Bench Mounting Rig type 1100P). It can measure filter efficiency, pressure drop and impact air flow. The device is possible to use for testing a high efficiency filters such as a HEPA filters. Parameters: test particles is NaCl; particle size: 0.002 – 2 μm; mean value of particle size is 0,6 μm; particle concentration is up to 13 mg/m^3; air flow 10 – 95 l/min, air velocity 1 – 9.5 m/min; test sample size 100 cm^2; filter sample thickness is up to 40 mm.

Table 1. The changing values of surface tension and conductivity with SnO_2/CrO_2 concentrations.

	Concentration of catalysts (%)				
Solution properties	0	1	2	3	4
Surface tension (mN/m)	51.24	55.73	57.09	57.71	62.84
Conductivity (μS/m)	610	486	587	512	478

Results and discussion

Properties of polymer solutions

We determined the changes of surface tension and conductivity of PU solution for different concentrations of SnO_2/CrO_2 (**Table 1**). There is an increasing of surface tensions of polyurethane solutions with growing of catalyst concentrations. The abrupt variations appear in conductivity with introduction of particles of metal's oxides, but for all concentrations conductivity reduces compared to unmodified solution.

Viscosity has increased with adding of catalysts (**Fig. 3a**). The variation of viscosity with share rate was observed. **Fig. 3b** demonstrates that viscosity decreases with increasing of the share rate for all solutions. It can be concluded that the introduction of metal's oxides particles has an influence on the properties of PU's solution. But as we will see in the next subsection, this influence has virtually no negative impact on the structural and dimensional properties of the future fiber layers at certain concentrations. So, the use of metallic oxides particles for the modification of polymer's solution in selected concentrations does not hinder the process of electrospinning.

Properties of produced fiber's layer's

There are SEM images of PU nanofibers containing 0; 1; 3; 4% SnO_2/CrO_2 respectively in the **Fig. 4**. Well-defined and bead-free nanofibers were obtained by electrospinning from colloidal solutions with various amounts of additives. We can observe the thickening of diameters for samples with 1 and 2% of catalytic agents. But there is no increasing in diameters with 3 and 4% of SnO_2/CrO_2 in comparison with unmodified nanofibers.

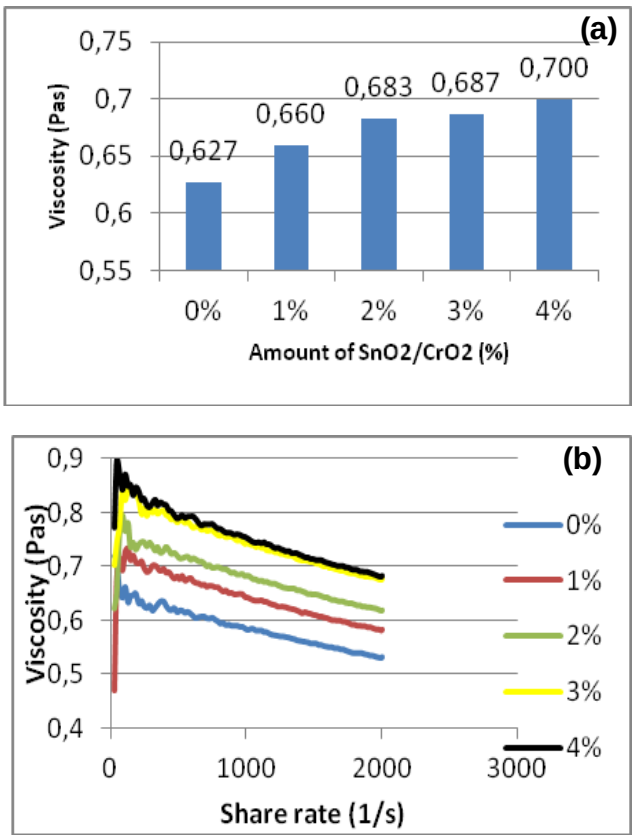

Fig. 3. (a) Dependence of the viscosity of the solution on the amount of catalyst; and **(b)** the change of viscosity with share rate for polyurethane.

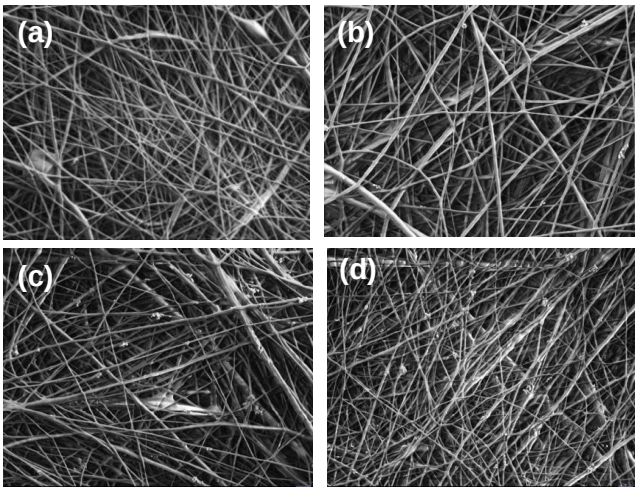

Fig. 4. SEM images of samples of PU (a) 0%; (b) 1%; (c) 3% and (d) 4% nanofibers includes various present of SnO_2/CrO_2 catalyst, (×5000).

These visual remarks are consistent with calculations of the average diameters with Lucia 32G computer software. 300 different measured values were used for each sample. The effect of catalyst concentration on the average diameter of polyurethane's fibers is in **Fig. 5**. We can trace an interesting tendency. The small concentrations of catalyst (1 and 2%) lead to the thickening of nanofibers, because the value of the average diameter for PU layers is 237nm. Similar values for samples with 1 and 2% of additive are 253 and 267nm respectively. But the

increasing of an amount of SnO_2/CrO_2 demonstrates the opposite effect: diameters of fibers with 3 and 4% of the metallic particles decreases by 18% in comparison with unmodified sample. Therefore, our additives in certain concentrations contribute to the production of thinner PU nanofibers.

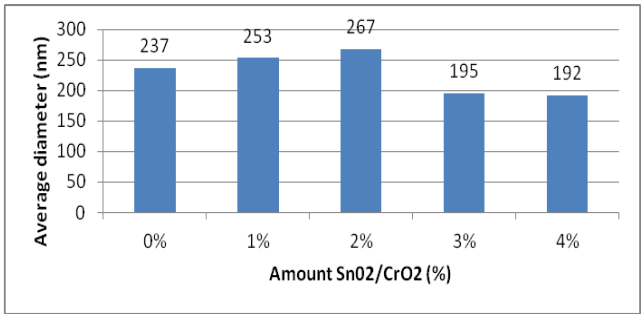

Fig. 5. Dependence of average fiber diameters on amount of SnO_2/CrO_2.

Fiber uniformity was determined using the number and weight average calculations. According to the results, number average and weight average of fiber diameter increase with SnO_2/CrO_2. Based on the computations presented in **Table 2** we can conclude that prepared fibers are fine and uniform.

Table 2. Results of fiber uniformity properties for samples with different amounts of modifiers.

PUR fibers	Fiber uniformity properties		
	Number average (An) (nm)	Weight average (Aw) (nm)	Fiber uniformity coefficient (Aw/An)
0%	237,38	250,8	1,05
1%	253,28	277,43	1,09
2%	266,53	288,95	1,08
3%	195,38	216,77	1,1
4%	192,59	212,37	1,1

To ensure that added particles are really present on the surface of nanofibers, SEM-EDS analysis was utilized for PU and modified nanofibers; the results are presented in **Fig. 6**.

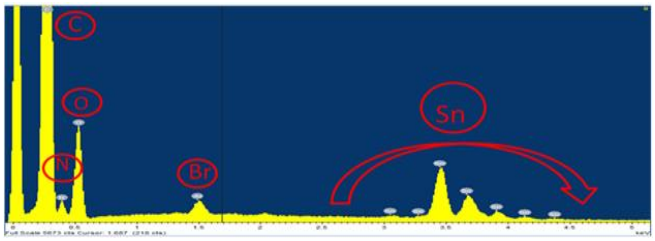

Fig. 6. Area EDS of the modified nanofiber mat with 4%SnO_2/CrO_2.

The presence of C, N, O, Br corresponds to the type of elements present inside the neat nanofibers. The extra peaks responsible for tin are also present. Indication of tin peaks from nanofiber surfaces by EDS analyses gives a confirmation that Sn particles can be carried out by cylinder body from dish with polymer solution during the electrospinning process. EDS maps showed us homogeneous distribution of Sn particles on the surface of fibers layer. In the **Fig. 7 a** location of green points corresponds with location of main catalyst agent for samples with 1 and 4% of SnO_2. Good particles distribution means that fiber's surface may provide catalytic activity, and the whole surface may be uniformly involved into the reaction process.

Then surface density of fiber layers for different concentrations of catalyst was calculated. According obtained data the surface density of 0% = 4,5 g/m², 1% = 3,82 g/m², 2% = 3,87 g/m², 3% = 4,57 g/m², 4% = 4,54 g/m²; consequently, when concentrations are 3 and 4%.

Measurements of catalytic activity

Catalytic activity was calculated as a ratio of the concentrations of emissions before and after the filter. Samples without catalysts have demonstrated some surface sorption of the NOx (**Table 3**). Modified samples exhibit the catalytic activity, capture NOx, CO and reduce the hit in the air of these harmful substances. The data demonstrated that with higher concentrations (until 3%) of SnO_2/CrO_2 bigger amount of pollutants were neutralized. With a subsequent growth of additive's amount up to 4% we observed the small decreasing of average catalytic efficiency. That is why the concentration 3% was selected as optimal for the modification of PU samples to impart catalytic properties.

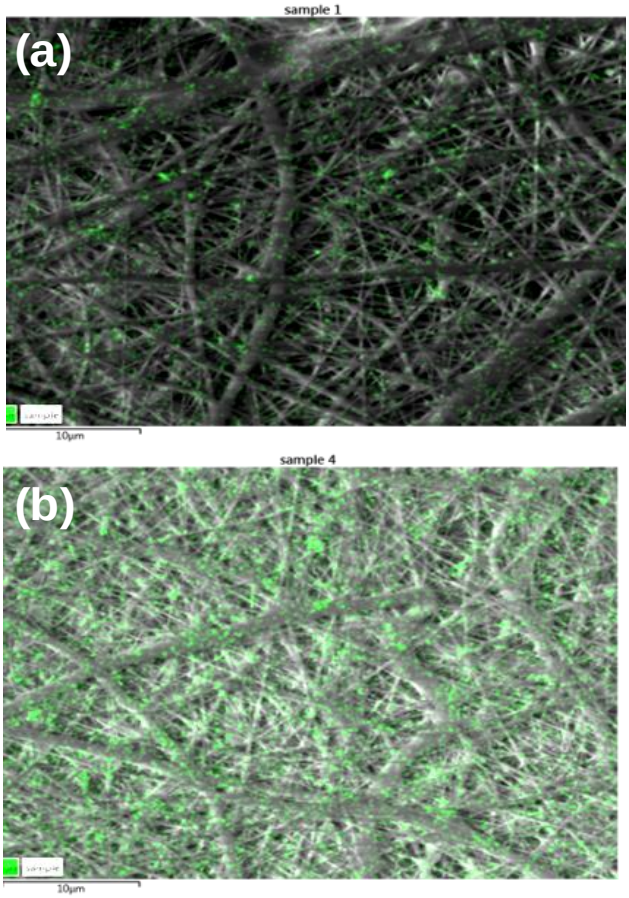

Fig. 7. Photos of fibers with color distribution of Sn particles on the samples surface.

Table 3. Average catalytic efficiency of samples during experiments

Filter	CO (%)	CO_2 (%)	NOx (%)
PUR	-3	1	1,5
PUR+1%S nO_2/CrO_2	46	34	40
PUR+2%S nO_2/CrO_2	49	42	41
PUR+3%S nO_2/CrO_2	81	75	73
PUR+4%S nO_2/CrO_2	79	73	72

In order to understand the difference in behavior between PU nanofibers and modified samples during contact with harmful gases we can analyze **Fig. 8**. There is an example of behavior of our samples in contact with CO.

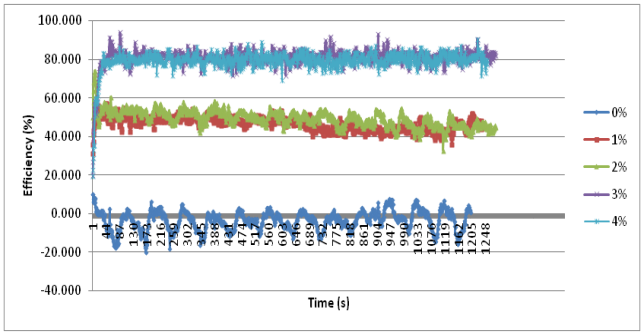

Fig. 8. Changing of catalytic efficiency for CO in time for PUR nanofibers with 3% of SnO_2/CrO_2.

The sample without catalyst does not demonstrate catalytic activity. But there is a low efficiency at some parts of the curve corresponding to 0% on the last graph. It is explained by the sorption of CO on the developed nanofibers surface. Samples with additives behaved differently. At the beginnig of this test catalytic activity gradually increased, reached the certain value, and then remained constant in time. All samples demonsrated a similar effect in the relation with NOx. There is no difference in the catalytic efficiency for nanofibers with 1 and 2% of SnO_2/CrO_2. The same conclutions can be done about the samples with 3 and 4% of additive. So, the sample with 3% of particles is the most successful from the point of view of efficiency and the quantity of used catalyst. Therefore PU nanofibrous layer with 3% of SnO_2/CrO_2 (95/5) is offered as a filtering material for the air-contidioning systems based on data about the structure, diameters of the fibers and the measurement of catalytic activities in the oxidation reactions of CO and NOx.

Conclusion

Results of present work are the fabrication of PU nanofibers, modified by particles of SnO_2:CrO_2 (95:5) in concentrations 1; 2; 3 and 4%. The simple modification process includes the introduction of oxides of catalytic agents into the polyurethane solution, stirring for 48 hours with followed producing of the nanofibers by the electrospinning technology with nanospider system. The properties of solutions were analysed before fiber foming. We found that PU/SnO_2/CrO_2 colloidal solution can be electrospun to form smooth nanofibers. The structure of the obtained fibers was studied with SEM. Photos and EDS analysis showed the presence of particles of used additives on the surface of fibers. Nanofibers with SnO_2:CrO_2 showed the catalytic activity in reactions with NOx and CO in comparison with samples of unmodified PU. When the concentration of catalyst increased from 2 to 3%, the catalytic activity also grew up. However, with further increasing of the concentration up to 4%, a slight recession in the efficiency was found. It became the main reason to choose 3% concentration as optimum for this catalyst. Achievements of this research are the choice of catalyst, which was not studied before, easy modification's process of the polyurethane nanofibers and the use of industrial technology for the production of modified nanofibers. It allowed to produce the multifunctional filtration material for the air purification from PM and emissive gases.

Acknowledgements

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