

ELECTROSPRAYED NANOPARTICLES FOR NANOFIBER COATING

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ABSTRACT

The paper presents experimental results of the combination of electrospinning and electro spraying techniques for the deposition of inorganic nanoparticles over polymeric nanofibers to create novel multifunctional nanomaterials. The process is designed for the formation of fibrous filters of enhanced collection efficiency in submicron range by covering the fabric with a catalytic material. The fibers made by PVC, polyamide, or polysulphonate (PSU) were covered with MgO, TiO₂ and Al₂O₃ nanoparticles. The obtained structures were porous at nanometer scale increasing total surface area of the catalyst. By this method polymer nanofibers of diameter smaller than 800 nm blended with metal oxides nanoparticles of the size 20 to 100 nm. This technique can be used for the production of masks, filters, or scaffolds in biotechnology.

INTRODUCTION

Electro spraying is a technique of liquid atomisation utilizing electrical forces by maintaining a capillary nozzle at high voltage. The droplets obtained by this method are charged and can be of microns size. The size of the droplets and their production rate can be controlled by changes the liquid flow rate and voltage [1-3]. This technique can be used for the production of nanoparticles, as a result of break-up of electrified jet when the low-viscosity solution is used. Electro spraying has been used to deposit ultra-thin films of inorganic, organic and biological materials, to generate nanoparticles and quantum dots, to sort them according to their sizes, and to help with dispersion and delivery of nanomaterials [4, 5]. Electro spray has found various commercial applications in the field of mass spectrometry, painting, inkjet printing, and recently in nanotechnology.

Electro spinning is a process of formation of nanofibers from a polymer (high-viscous liquid), by electrical shear stress [6, 7]. During electro spinning, polymer solution is forced through a spinneret under the influence of high electric field. The resultant liquid jet evaporates under controlled temperature and humidity, and remained semi-solid polymer fiber is deposited onto a collector. The deposition rate of nanofiber varies from 2 m/sec to 200 m/sec depending on the physical properties of solution and processing conditions.

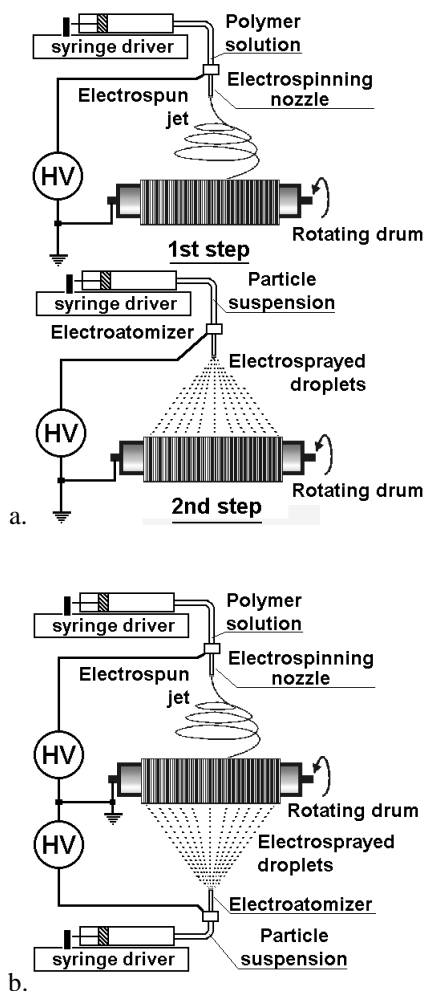
Combined electro spraying with electro spinning techniques can solve the existing unsolved problems of electro spinning technique in large areas of applications ranging from catalysis, defense to biotechnology.

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EXPERIMENTAL

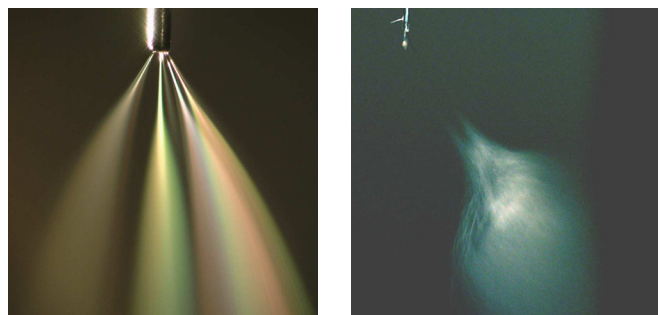
The electro spinning system comprised a stainless-steel capillary nozzle and an aluminium foil (10 µm thick) stretched over an aluminium rotating drum. The diameter of the drum was 60 mm. The rotational speed of the drum was about 500 rpm. The diameters of the capillary was 0.45 mm o.d. When electro spinning nozzle operates alone, it was positioned vertically. The distance between the nozzle tip and the drum was changed depending on polymer, from 80 mm (PSU) up to 110 mm (PVC). In the simultaneous electro spraying/electro spinning process, the electro spinning capillary nozzle was placed horizontally. The capillary used for electro spraying was 0.7 mm o.d. The distance between the nozzle tip and the drum was 50 mm. For post-spinning deposition system the electro spinning nozzle was connected to a high dc voltage supply SPELMANN SL600W/40kV/PN of positive polarity. For simultaneous electro spinning and electro spraying system negative polarity was used. The drum was grounded in each case. The electro spray nozzle was connected to the high dc voltage positive polarity provided by SPELMANN SL300W/30kV/P.

A solution of 9 wt % PVC dissolved in mixture of DMF (Dimethylformamide) and THF (tetrahydrofuran), and solution of 20 wt % PSU dissolved in DMF were prepared via overnight stirring at room temperature. The polymer solution was then loaded into a syringe fitted to a syringe pump. Electro spinning was carried out at room temperature in air with relative humidity of 45-50 %. The electro spinning process was carried out by 12 kV (PVC, PSU) and 18kV (nylon), and 1 ml/h flow rate of polymer solution.



RESULTS

Two main configurations of electrospaying/electrospinning systems have been tested (Fig. 1): consecutive electrospinning of polymer solution followed by electrospaying of nanoparticle suspension (Fig. 1a), and simultaneous electrospinning of polymer solution and electrospaying of nanoparticle suspension (Fig. 1b).



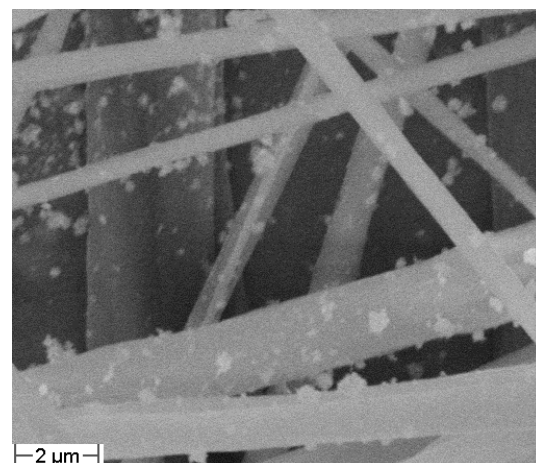
a. Multijet mode. Metanol with TiO₂ nanoparticles (concentration 0.6 wt.%); Electrode distance 11 cm; Flow rate 1 ml/h; voltage 10 kV
 b. Electrospinning PVC in DMF and THF (concentration 9 wt.%); Electrode distance 5 cm; Flow rate 0.5 ml/h; voltage 12 kV

Fig. 2 Examples of spray and spinning plumes

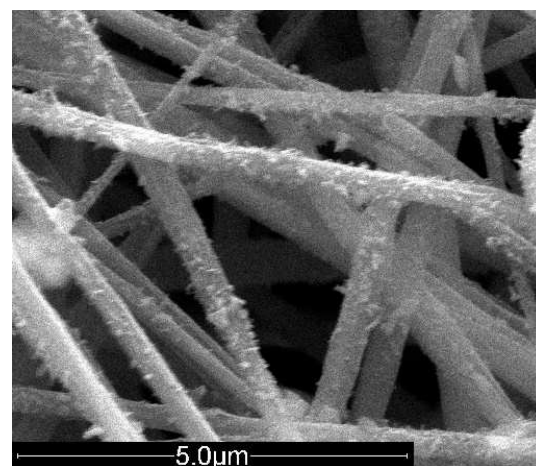
Fig.1 Experimental setup a) Electrospinning followed by electrospaying in a separate process (post-spinning deposition), b) Simultaneous electrospinning and electrospaying from two capillary nozzles

Before deposition, the particles were stirred for a time of 2 h in methanol with an addition of a surfactant Dynasylan ® Memo in order to stabilize the suspension. The particle suspension was electrospayed for the voltage of 8 kV, and flow rate of 0.5 ml/h. The voltage and flow rate were adjusted for each suspension in order to obtain stable multijet mode. The spray plumes were recorded using CCD camera Panasonic NV-GS400. The nanoparticles of metal oxides, such as MgO, TiO₂ and Al₂O₃, suspensions in methanol were used in all these experiments. Methanol was supplied from POCH Gliwice (Poland). MgO particles of size 100 nm, TiO₂ mean diameter 29 nm, and Al₂O₃ particles of mean diameter 30 nm were purchased from Alfa Aesar. DMF and THF were supplied from Chempur (Poland). The suspensions were electrospayed for a time of about 60 minutes in the process of post-spinning deposition. The production of nanocomposite materials in the process of simultaneous electrospinning and electrospaying from two capillary nozzles took also a time of about 60 min. The percentage of nanoparticle in the nanocomposite membrane was found to be about 3 %.

The morphology of nanocomposite materials produced by electrospinning and electrospaying was tested under a scanning electron microscope Zeiss EVO-40 or FEI Quanta 200.



a.



b.

Fig. 3 SEM images of the fibers with deposited nanoparticles by electrospaying on a PVC fiber. Concentration 0.6 wt.%. Multijet mode. a. Simultaneous electrospinning and electrospaying. Fiber smaller than 800nm dia. b. Postspinning deposition. Fiber 600nm dia.

In the first configuration, the electrospun fibers were deposited onto a substrate (Al foil) covering a rotating drum, and after the process was completed, the electrospin nozzle was replaced with electro spray nozzle dispersing nanoparticle suspension. In the second configuration, two separate nozzles were used over a rotating drum. The nozzle electrospun the fibers was placed horizontally and the electro spray nozzle vertically above the drum. In each case, after the particles were deposited, the fabric was dried in slightly elevated temperature, for example, to 50°C before its inspection under a scanning electron microscope.

In the presented experiments, the nanoparticle suspension in methanol with Dynasylan® Memo surfactant was electro sprayed and deposited onto electrospun polymer fibers. Examples of spray plumes, the multijet modes of electro spraying and electro spinning of PVC solution are shown in Figs. 2a and 2b, respectively. In the multijet mode, the droplets are small and allow generation smaller particles. In the following, the presented results were obtained for the multijet mode. Low particle concentration and ease of evaporation of the solvent enabled the deposition of particles on the fibers. The morphology of the layer differs depending on the structure of deposited particles.

The SEM images of the fibers with deposited nanoparticles are shown in Figs. 3 – 6. Two examples of electrospun fibers of PVC electro sprayed on rotating drum with incorporated MgO nanoparticles are shown in Fig. 3. Fibers deposited onto rotating drum are straight, more uniform in diameter and are evenly deposited onto a substrate than those deposited onto a flat plate (not shown). This technique was therefore further used for the production of nanocomposite fibrous mats.

PVC fibers with deposited MgO particles shown in Fig.3 were obtained by simultaneous electro spinning and electro spraying method (a) and by postspinning deposition (b). Similar SEM photographs but for Al₂O₃ and TiO₂ particles deposited onto PVC fibers are shown in Fig. 4 and 5 respectively. It can be noticed that the particles on the fiber form agglomerates built of single crystallites.

From these experiments results that postspinning deposition forms denser deposit of particles on the surface of the mat, but in simultaneous electro spinning-electro spraying the particles are more uniformly distributed within the fiber layers. In Fig. 6 are shown two fabrics obtained from various materials: PSU and nylon. No significant difference in the process of particle deposition was noticed.

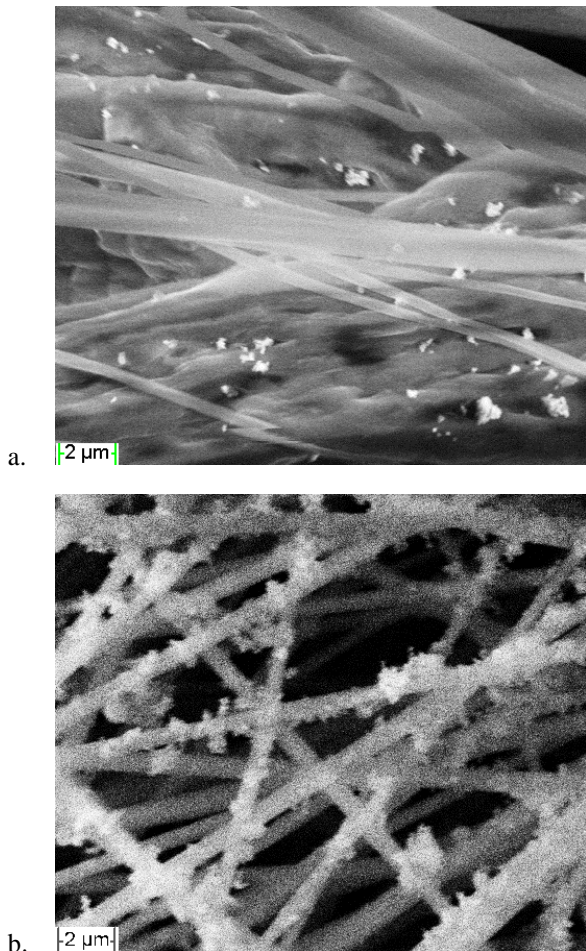


Fig. 4 SEM images of the fibers with deposited Al₂O₃ nanoparticles by electro spraying on a PVC fiber. Concentration 0.6 wt.%. Multijet mode. a. Simultaneous electro spinning and electro spraying b. Postspinning deposition. Fiber 600 nm dia.

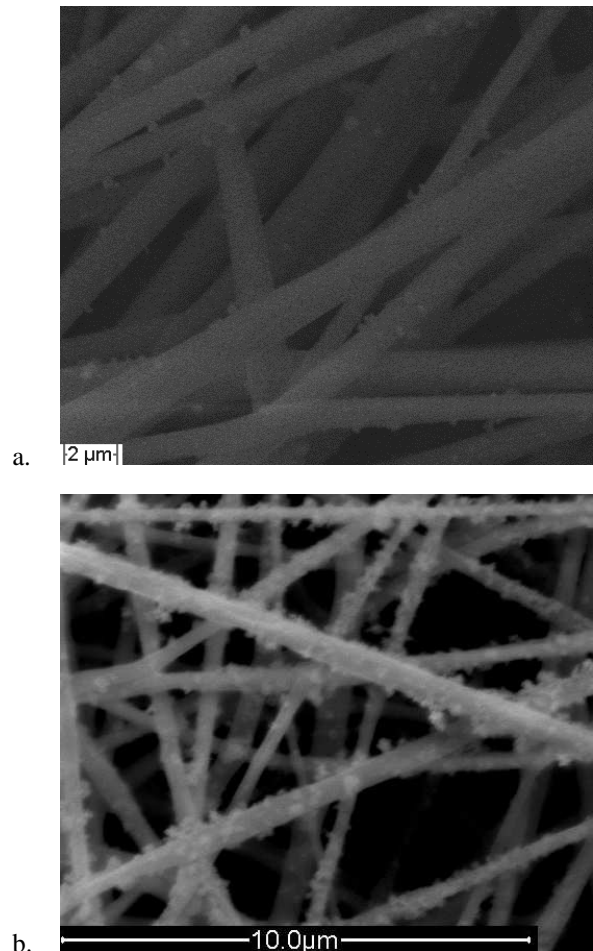


Fig. 5 SEM images of the fibers with deposited TiO₂ nanoparticles by electro spraying on a PVC fiber. Concentration 0.6 wt.%. Multijet mode. a. Simultaneous electro spinning and electro spraying; Fiber 600nm dia. b. Postspinning deposition. Fiber 600nm dia.

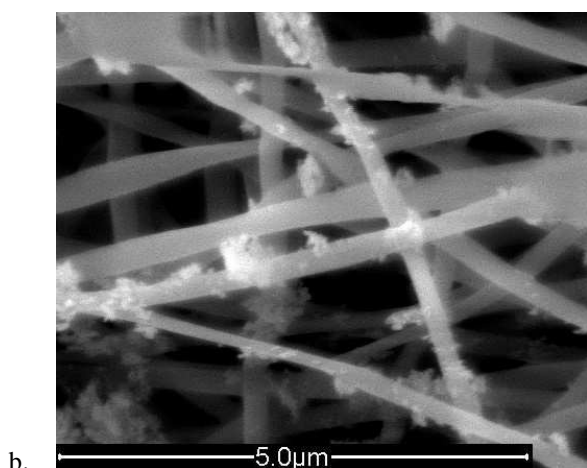
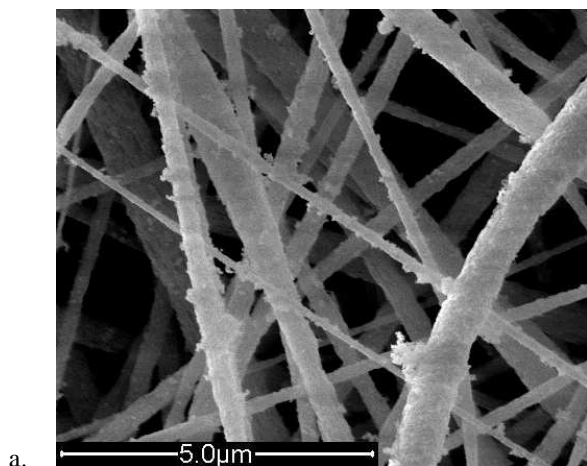


Fig. 6 SEM images of the fibers with deposited nanoparticles. a. TiO_2 particle deposited by electrospaying on a PSU fiber 600 nm dia. Concentration 0.6%. Multijet mode. Postspinning deposition; b. TiO_2 particle deposited by electrospaying on a nylon fiber 400 nm dia. Concentration 0.6%. Multijet mode. Postspinning deposition.

SUMMARY

The paper provides experimental results of electrospay deposition of nanoparticles of metal-oxide on a PVC, PSU and nylon fiber. The obtained structures are porous at nanometer scale increasing total surface area of the particle catalyst. The reason for choosing electrospay is that electrospay is a single-step, low-energy, and low-cost material processing technology which can operate at atmospheric conditions with easily controlled deposition rate and coating thickness via voltage and flow rate. The materials are not damaged after the spraying and spinning processes.

This technology can be applied for the production of filtration mats with improved efficiency by incorporated catalytic material, electrodes of high specific surface area for fuel cells, or scaffolds for tissue regeneration.

Filter mats produced from electrospun fibers enable gas flow through the filter. When catalytic materials is deposited onto the fibers, the mat can operate as simultaneous nanoparticle filter and harmful-gases removing device.

It was also observed that the multijet mode is more effective in nanofibers coating resulting in denser and more uniform coverage of the fibers.

ACKNOWLEDGMENT

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