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Microreactors with embedded nanofibres manufactured by electrodynamic focusing

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Abstract

This work shows a simple way of producing fixed bed microreactors or packed microcolumns by using electrodynamic focusing. Based on previous results that showed fibre focalization on orifices is possible, we explored this technique to electrospun fibres inside microchannels. Different polymeric nanofibres - either neat or composite, i.e. fibres containing particles - can be deposited without meaningful difference on deposition parameters, resulting in packed structures. Moreover, distinct substrates can be used for mask production, which can be reused with the respective setup. Finally, the use of a dry process shortens the process time, increasing productivity.

Keywords: Electrospinning; electrodynamic focusing; microreactors; nanofibres.

1. Introduction

Miniaturization of chemical engineering unit operations and chromatographic microcolumns, for application on chemical synthesis or sample analysis respectively, is an important trend due to economic and environmental issues [1]. The production of fixed-bed microreactors can benefit from the use of small particles/constrictions that increase the surface area [2]. On the other hand, miniaturization increases pressure drops and diminishes flow rate; thus, for microreactors, these can be counterbalanced by the use of a microfibrous catalyst structure instead of catalyst pellets [3]. A simple way to increase surface area and simultaneously produce a fibrous material is the use of micro and nanofibres. These fibres can be produced by several processes. However, electrospinning presents some advantages, such as low cost and a setup that is simple and easy to build. Furthermore, it is possible to produce fibres from various polymer solutions as long as they have adequate viscosity. The fibre surface can be modified by electroless metal deposition and different kinds of particles can also be incorporated into the polymeric solution aiming at modifying fibre performance [4,5]. The use of electrospinning in the direct production of nanofibres inside small dimensions is complex due to the intense electric fields formed on acute angles on the devices topography that concentrate electrostatic charges and drive the formation of nanofibres away from the constricted areas [6]. A conventional approach [7] is the deposition on a plane surface and the device itself is designed on a second substrate, also used for device sealing. Using this method, polymeric fibres were not preserved due to calcination and sealing steps. Production of nanofibres inside orifices, as developed by Salim [8], requires a time consuming method,

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expensive reactants and complex equipment. Moreover, no attempt was done on deposition inside microchannels or more complex microstructures, such as microfluidic oscillators [9]. This is relevant because such structures asymmetric channels are quite common, and can hinder a homogeneous fibre deposition. However, microfluidic oscillators, whether or not packed with adsorbent materials, may very likely be turned into interesting microreactors. Usually, microchannels are made only on few types of substrates according to the application [1], but, as the fibre must be electrospun over a grounded substrate, metal and silicon facilitate the electrospinning process. Also, the substrate has to be plane in order to allow the sealing process, which favours silicon that is inert for thermal cycles up to 500°C.

In conventional electrospinning process, the fibres follow the electric field lines and deposit mainly over the outer surface [6]. In order to circumvent this effect, we deposited nanofibres using the electrodynamic focusing process [8], which allows to direct the electric field lines through orifices of metal masks, depositing nanofibres in selected areas of the substrate. Normally, both the masks and the microstructures are defined by conventional microelectronics processes which involve several costly and time consuming steps and also require facilities such as cleanrooms [8]. In this paper, an innovative procedure was established to produce the masks and the microstructures, using materials, techniques and equipment normally applied for prototyping printed circuit board (PCB). Although for more than two decades the use of PCB technology was common on the development of Microsystems [10], it is unusual using silicon as substrate. Moreover, PCB technology presupposes the use of wet processes and lithographic masks; however, this paper point out to a single completely dry step. So, in the development of this process the microstructures and the masks were cut by laser using a prototyping PCB machine. Microstructures and masks were developed using CAD software, which resulted in shorter time and less use of materials and resources. Different types of polymeric solutions were investigated, some including the addition of materials that can improve adsorption, aiming to investigate their effect in the characteristics of the electrodynamic focusing process [8] and their potential as a material integrated in a microreactor. Thus, the aim of this work was the development of a simple process, with few steps, for deposition of fibres inside microchannels and miniaturized structures in order to produce packed microcolumns or fixed bed microreactors.

2. Experimental

2.1. Mask and mask + substrate testing

Two different sets of masks were designed by CAD, the first one mainly to test electrodynamic focusing parameters and the second one for nanofibre deposition inside microchannels. For the first set, three different designs were developed in order to evaluate mask behaviour during the electrodynamic focusing process. Fig. 1 shows the schematics of the three masks. The array of orifices seen in Fig. 1 a) is the commonest shape of microreactors [11]. Curved microchannels are used for several unit operations such as mixing, microcolums and preconcentration devices [12] - Fig. 1 b) presents several cyclic microchannels. One orifice was placed in the centre in order to test electrical interference during fibre electrodeposition. Fig. 1 c) shows typical microfluidic oscillators [9]. The second set, as seen in Fig 1 d), also shows curved structures, the "S" shape is important for mixing or reaction [13], and straight channels, a common approach for heating and mass transfer [12].

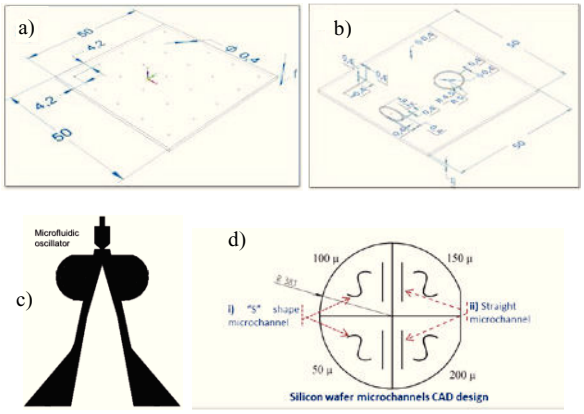

Fig. 1. CAD design: a) Array of orifices, b) Curved microchannels, c) Microfluidic oscillators and d) Set of i) "S" shape and ii) straight microchannel.

The first set of masks were produced with a thin copper layer (70 µm thick) as mask, that was attached to the substrate (silicon), using LTCC (DuPont, 240 µm thick) as spacer and conventional tape as sealing. In the second set, the masks were produced using copper-clad laminate (Formiline, FR-4 type, copper foil of 35 µm and 74 µm of total thickness). The microchannels were made in silicon wafers (100). Masks and devices were produced in a laser cutting machine (LPKF ProtoLaser U3, 355 nm laser, spot 15

microns). The channel in the silicon wafer was evaluated by profilometry (3030 Veeco Instruments Inc. USA) and the diameters and morphology of the fibres were measured by optical (Leica S8AP0) and electro scanning (Nova Nano SEM 400 FEI, USA) microscopies. For depositing the fibres inside the microchannels, the apparatus was assembled aligning the aperture in the mask with the channel in the silicon wafer. The set was mounted on a grounded metal substrate.

2.2. Setup for fibre deposition

In order to perform electrodynamic focusing, the fibres were electrospun using a modified conventional electrospinning setup [5] with two high voltage sources. A voltage of 400 or 600 V (Stanford Research System Inc, 0 - 1.2 kV) was applied to the mask, depending on the process and on the polymer to obtain the nanofibres. A syringe (5 mL) with a hypodermic needle attached (0.70x25 mm) was filled with the polymeric solution, and 5 or 10 kV was applied to the needle using a high voltage power supply (Gamma High Voltage Research, Inc., 0 - 30 kV). Fig. 2 depicts a schematic view of the optimized electrodynamic focusing setup, including the substrate with the attached mask.

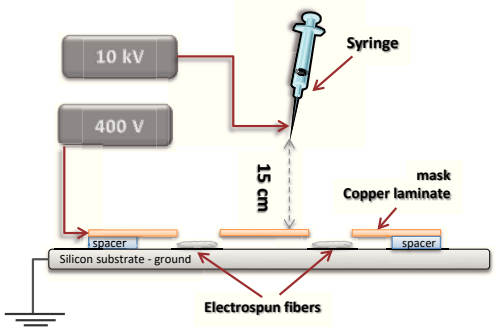

Fig. 2. Schematic view of the electrodynamic focusing setup and important settings.

2.3. Materials and methods

Nanofibres were electrospun from three different solutions: 6% polyacrilonitrile (PAN) dissolved in N,N - dimethylformide (DMF); 18% polyvinylidene fluoride (PVDF) dissolved in a mixture of 3 parts of acetone and 1 part of DMF, and 20% polivinylpirrolidone (PVP) dissolved in deionized water. All solutions were stirred during 12h. Additionally, four different dispersions were obtained using PAN/DMF or PVDF/DMF mixed with copper phthalocyanine or carbon black in a particle/polymer concentration of 1:1 (wt.%). All the reagents were purchased from Sigma-Aldrich and used as received.

2.4. Simulation

Simulation used Comsol Multiphysics®, considering electrostatic mode and variable boundary conditions on the wall surfaces.

3. Results

3.1. Masks and microchannel production

Fig 3 a) presents photos of the main produced masks using copper foil as substrate, showing that the laser tool provides a sharp and smooth cut. This is mandatory because, due to the high voltage, short circuits near sharp tips must be prevented. Furthermore, sharp edges on complex structures, as microfluidic oscillators, were preserved. Since the copper foil is thick, the produced mask is self-sustained and can be used several times. Similar results were obtained with copper clad (FR4) substrate, as can be seen in Fig 3 b).

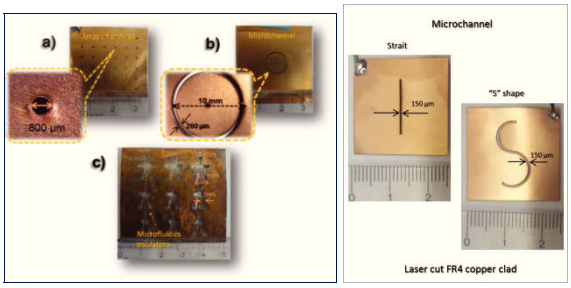

Fig. 3. Photos of the laser produced masks: a) on copper foil, and b) on FR4 copper clad.

The silicon microchannel produced by laser showed rough surfaces on both bottom and sidewall surfaces with evenly spaced irregularities, due to laser spot size, as shown in Fig. 4. The bottom roughness, due to increased surface area, can be useful for fibre adhesion. The vertical irregularities however can increase preconcentration effects because this type of irregularity usually creates fluid preferential paths that may favour gaseous sample liquefaction in the constricted areas [14].

The channel size obtained by profilometry on silicon was 150 µm x 13 mm (width x length) with a depth of 150 µm, confirming that the laser cutting process is efficient for producing microchannels on silicon wafers, allowing the electrodeposition of micro and nanofibres.

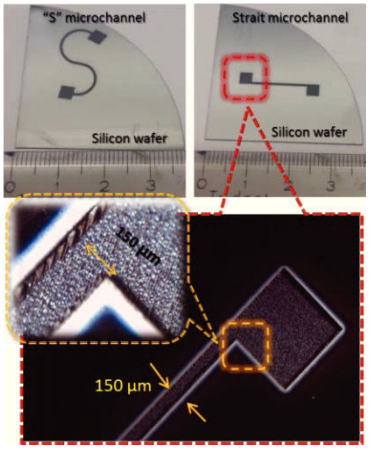

Fig. 4. Microchannels on silicon wafer produced by laser cutting. Detail of irregularities produced by laser spot.

Despite the fact that the channel surface resulted rough, this new process allows a faster production of prototypes compared to conventional silicon microfabrication processes such as anisotropic etching.

3.2. Electrodynamic focusing

The first set of masks (Fig. 1) was assembled over silicon wafers in order to evaluate their feasibility in electrodynamic focusing. Simulation and experimental results are shown in Figs. 5 and 6.
Fig. 5 shows optical images of one of the orifices from the mask presented in Fig. 1 a). In Fig. 5 a) the focus is placed on the surface of the copper foil and no fibres are observed which indicates that these fibres are mainly collected on the silicon substrate. Fig. 5 b), that has the focus on the substrate, shows the fibres collected mainly on the centre of the mask. The fibres are only weakly attached to the mask and its removal does not result in meaningful loss of fibres as can be seen in Figs. 5 c) and d).

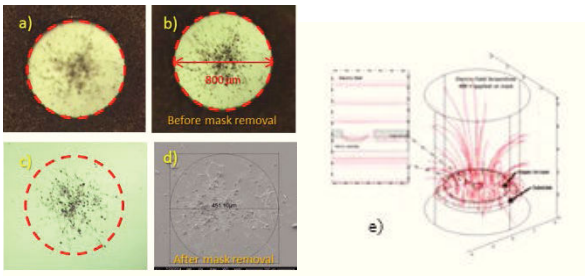

Fig. 5. Optical images of one of the orifices: a) focus on the surface of the copper foil, b) focus on the substrate, c) after mask removal, d) SEM spot of collected fibres, e) simulations: electric field streamlines. Detail: arrows → normalized electric field vector.

Simulation results show good agreement with the experimental measurements (Fig. 5 e)). The simulation considered 70 µm copper foil as mask, silicon as substrate and air as insulator. In Fig. 5 e) there is a high concentration of electric field streamlines in the orifice but the more intense electric field is found in the centre (see detail). Hence, the electric field can be considered focused which favours deposition on the centre of the structure. The simulations also demonstrate that, if the whole wall is a metal, it contributes to direct field lines, leading them to concentrate in the centre of the hole, a very important result that confirms the feasibility of copper foil as mask.

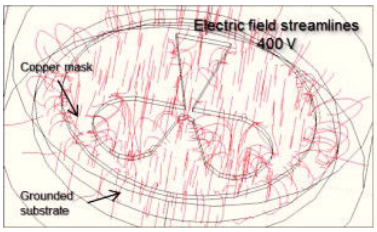

Fig. 6. Simulation of the electric field in the copper mask considering 400 V applied on the mask and 10 kV in the needle. It is not possible to see the needle due to the distance to the collector.

Similar results were obtained when the microfluidic oscillators were simulated, as shown in Fig. 6. The simulations show the field lines into the centre of the opening, even when its contour is non-symmetrical. Fig. 7 shows obtained electrospun fibres concentrated in the centre of the mask.

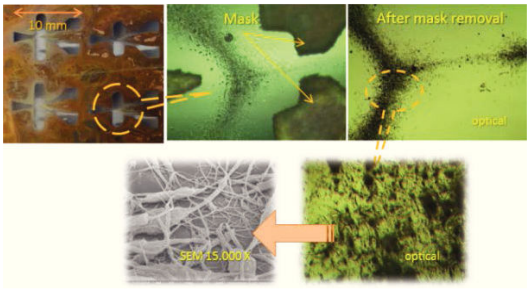

Fig. 7. Electrospun fibres concentrated in the mask centre of microfluidic oscillators, in agreement with simulation.

3.3. Microchannel production and testing

The FR4 laminate mask and the microchannel in silicon wafer were aligned in order to electrospun the fibres inside the channel by electrodynamic focusing. In this case, the resin impregnated fibreglass acts as spacer and insulator. The mask was attached to the silicon wafer and the resulting set was mounted on a

grounded metal substrate. The process was performed with the PVP solution with or without added carbon black particles. It was observed that the nanofibres reach the bottom of the cavity as can be seen in Fig. 8 a).

The optical microscopy images of fibres within the cavity, with and without the addition of carbon black, are shown in Figs. 8 b) and c). Particle incorporation can be confirmed by the presence of dark spots in the fibres (Fig. 8 c)) which demonstrates that the electrodynamic focusing technique is effective whether or not particles are inserted in the dispersion.

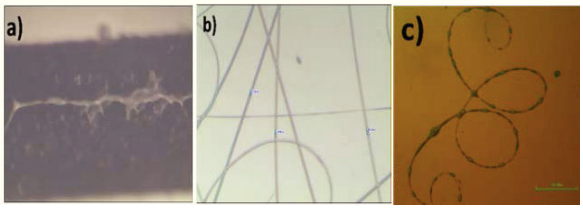

Fig. 8. a) Electrodeposited fibres within the microchannel, b) Image fibre without carbon black, c) Dark spots confirms the incorporation of carbon black in the fibre.

3.4. Characteristics of the fibres

Table 1 presents the average diameter of fibres obtained with either electrospinning process. A general tendency of smaller diameters with the electrodynamic focusing process can be attributed to the high electric fields present near the substrate, which may deform the fibre and also facilitate solvent evaporation. Similar situation can be seen on fibre formation with two parallels electrodes [15].

Table 1. Comparison between the average fibre diameters.

Polymeric solution	Particle	Average fibre diameters (nm)		
		Conventional electrospinning	Electrodynamic focusing	d_{ratio}
PAN	pristine	340	381	1.12
	Phtalo	724	396	0.54
	Carbon black	160	176	1.10
PVDF	pristine	420	148	0.35
	Phtalo	500	115	0.30
	Carbon black	390	77	0.20

$$d_{ratio} = \frac{diameter\ electrodynamic\ focusing}{diameter\ conventional\ electrospinning}$$

The effect of diameter decreasing is more pronounced in PVDF samples probably due to the high polarity of fluorine radicals. A high polar interaction between particle and fibre, as can be found with PAN/starch particles composite [16], can drive the polymer molecules mainly to particle surface, which depletes polymer concentration nearby the particle and leads to thinner fibres.

Fig. 9 shows typical results of fibres obtained using different polymers. Fibres obtained using PAN or PVP result long, uniform, and spiralled, differently from the ones obtained using PVDF, which are very irregular and present many beads. The beads are associated with the low viscosity of the PVDF solution. Any dispersion containing carbon black or copper phtalocyanine does not influence the focalization of the fibres but, as expected, causes the formation of agglomerates. Thus, the application of the electrodynamic focusing setup does not severely influence the morphology of the fibre.

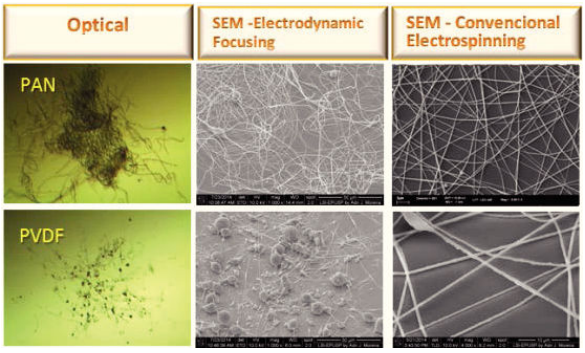

Fig. 9. Optical and SEM images of electrospun fibres obtained with different polymers and particles dispersed in solution.

4. Conclusions

A new approach was proposed for the electrodynamic focusing method, producing the masks and microchannels using laser cutting, aiming at producing a fixed bed microreactor and packed microcolumns. It was demonstrated that the electrodynamic focusing process allows electrospun nanofibre growth inside several microstructures, such as microfluidic oscillators, microchannels and cavities, using different polymeric solutions and polymer/particles dispersions, i.e., the masks shapes does not interfere in the process. The deposited fibres by electrodynamic focusing do not show noticeable morphological differences although the diameters may be different if compared to that obtained by conventional electrospinning. Thus, the feasibility of our method relies on low cost, one single cycle that is not time or reactant consuming.

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