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An innovative and versatile approach to design highly porous, patterned, nanofibrous polymeric materials

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Abstract Electrospinning technology is attracting increasing interest for the fabrication of several polymeric and inorganic nanofibrous materials useful for a wide range of applications. Although the intensive research performed to understand the physics of the electrospinning process, control of polymeric jet path and of fibre deposition still remains a challenge. In this work, micropatterned electrospun materials with tunable porosity are fabricated by using novel collector devices made up of a steel sheet coated with a vitreous enamel layer. The novel approach permits to modulate electrical properties of the collector, acting on charge distribution and charge diffusion properties of the vitreous enamel coating, without introducing substantial modification of the electrospinning apparatus. The proposed solution allows the achievement of novel electrospun products for all those advanced applications requiring materials with suited fibre deposition such as, microelectronics, optical and photonic devices, as well as scaffolds for tissue engineering.

Introduction

The use of electrostatic fields to generate fibres dates back to the first Formhals patent issued in 1934 [1], although only recently electrospinning found widespread interest for the production of continuous fibres with diameters ranging from nanometres to micrometres [2–8]. Electrospun nonwoven fabrics have been developed for a wide range of applications [3, 5, 8, 9], including scaffolds for tissue engineering, high efficiency filtration devices, selectively permeable materials for protective clothing, reinforced composite materials, catalyst supports, electronic devices, etc.

Notwithstanding simplicity of experimental electrospinning setup, an intensive research has been directed towards the understanding of the basic principles of this complex electro-fluidodynamical process and many studies have been reported on the physics of electrically driven jets in order to model the evolution of the jet instability [10–13]. A practical consequence of the fluid instability is the chaotic path of the jet that leads to a poor control of spatial distribution of the collected fibres. Control of the jet path and of fibres alignment has been faced by several researchers mainly focusing on two interrelated aspects: design of the target collector and manipulation of the electrostatic field acting on the system. Teo and Ramakrishna [7] provided a comprehensive review of many techniques employed to align fibres. In the most common approaches, the fibre collector is a static metallic frame with a proper geometry [3, 5], or a high speed rotating tool, e.g. a cylinder or a sharp-edged disc [3, 5, 7, 14, 15]. In other approaches, a high degree of fibre alignment has been achieved through manipulation of the electrostatic field acting on the fluid jets by using as collectors: (i) parallel conducting silicon strips spaced apart by a gap [16–18],

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(ii) multiple gold electrodes deposited on quartz wafers [16] and (iii) auxiliary guiding electrodes [19–22]. Fibre patterning has been achieved by using conductive collectors with insulating regions of different areas and geometric shape [23], or conductive grids [24, 25], although obtaining more complex patterns still remains a challenge. Moreover, almost all approaches applied so far present some limitations because a complex design of the electrospinning apparatus is often required; in addition, the patterned area is usually limited and only short collecting times are allowed, thus preventing the achievement of large and thick fibrous mats.

Another challenging topic in electrospun mat fabrication is the control of porosity, in terms of both pore dimension and fibre packing density. Pore dimension has been controlled by concurrent electrospinning fibres with micro and nano-scale diameter [26], or by using a salt leaching procedure [27], whereas an increase of fibre packing density has been achieved by substituting metallic collectors with composite collectors composed of a conductive substrate covered by a non-conducting layer [5, 28]. However, in this case, the non-conducting surface limited the collecting time, thus the electrospun mat thickness [29].

Here, we show that by using novel and versatile electrospinning collectors both targets discussed above, i.e. nanofibre patterning and control of fibre packing density, can be achieved. A peculiar aspect of this work is that no substantial modification of the electrospinning apparatus is required and the innovation arises from the combination of an old technology (electrospinning) with an ancient material (vitreous enamel). Although it has been used for centuries for standard low-tech applications (e.g. as corrosion protection in kitchenware, household equipment, chemical equipment, and pipes), enamel is a material that can be suitably engineered for advanced technological purposes. Vitreous enamel contains a great number of chemical elements from different sources. The main raw materials used in enamels are refractories (quartz, feldspar, clay) and fluxes (borax, soda ash, cryolite, fluorspar), together with opacifiers, colours, floating agents and electrolytes [30–32].

This article shows for the first time that vitreous enamel is a very promising material for electrospinning collecting devices owing to its intrinsic properties. The main interest for coupling electrospinning technology with vitreous enamel is related to enamel electrical properties. Indeed, vitreous enamel is a dielectric material characterized by high electrical volume resistivity (10^{13}–10^{19} Ω cm), thus being insulator at room temperature. Alkaline oxides have the largest effect on enamel electrical resistivity: the higher their content, the lower the resistivity. Indeed, alkali metal cations are the actual charge carriers, whereas the anions do not take part in current transport [31, 32]. In particular, sodium and lithium ions, having high diffusion rates, increase leakage current through the dielectric more than potassium, rubidium or caesium ions. Therefore, enamel electrical properties can be modified by varying the chemical composition, and in particular, the content of the alkaline oxides. In addition, electrical resistance of vitreous enamelled substrates can be easily modulated by a proper selection of the enamel coating thickness [32].

Materials and methods

Enamelled collectors preparation

Enamel raw materials were prepared by using a home-made frit with the following composition in wt%: SiO_2: 43, Al_2O_3: 1, B_2O_3: 13, Na_2O: 8, K_2O: 5, ZnO: 1, TiO_2: 22, P_2O_5: 3, F_2: 4, which gives a final white colour coating. Enamel raw material for Type A collectors, which were manufactured by means of dry-electrostatic application, was prepared by milling the frit for about 11 h in order to obtain a powder that was deposited electrostatically over a 0.8-mm thick steel sheet. Enamel coating thickness was controlled during the deposition process and collectors with different enamel thickness (150, 250, 350, 380, 530 μm) were prepared. The coated specimens were fired in a radiant furnace with oxidizing atmosphere at 850 °C for 6.5 min (standard firing condition). Type B collectors were prepared through a wet-spray application. Enamel raw material for wet application was prepared by milling for 4 h the frit in water and by adding, during the milling process, a montmorillonite clay (Mullenbach & Thewald GMBH, Germany, particle size ca. 50 μm) as doping material. The wet-milling process enabled the formation of a blend containing the suspended clay particles. Wet-enamel was sprayed over the steel sheets and dehydrated. Enamelled specimens with a coating thickness of 0.2 μm were obtained. The coated specimens were fired in a radiant furnace in the standard firing conditions. Type C collectors were manufactured by deposition of γ-alumina (45 ± 4 μm) on local regions of unfired Type A collector (150 μm) and then firing at the standard conditions. Type D collectors were obtained by applying a serigraphic paste containing 40% v/v graphite, over local areas of Type A enamelled specimen (150 μm) and then re-firing the modified surface at 720 °C for 6 min.

Electrospinning experiments

Poly-L-lactic acid (PLLA, Lacea H.100-E) ($M_w = 8.4 \times 10^4$ g/mol, PDI = 1.7) was supplied by Mitsui Fine Chemicals, Dusseldorf, Germany. Dichloromethane (DCM) and dimethylformamide (DMF), purchased by Sigma-Aldrich

Co., were used without any further purification. The electrospinning apparatus, built in house, was composed of a high voltage power supply (Spellman, SL 50 P 10/CE/230), a syringe pump (KDScientific 200 series), a glass syringe, a stainless-steel blunt-ended needle (inner diameter: 0.84 mm) and a grounded enamelled collector. A PLLA solution (13% w/v in DCM:DMF 65:35 v/v) was electrospun using the following experimental conditions: applied voltage = 12 kV, needle to collector distance = 15 cm, solution flow-rate = 15 × 10^{-3} mL/min, room temperature and relative humidity = 40–50%.

Characterization

Electrical conductivity measurements of enamelled electrodes were carried out according to standard IEC 60167. The detection area (700 mm^2) was circular and surrounded by a grounded guard electrode aiming at neglecting the contribution of surface conduction current in measurement of the bulk conduction current. Tests were performed at 25 °C and with applied voltage of 1,000 V.

Scanning electron microscope (SEM) observations were carried out using a Philips 515 Microscope at an accelerating voltage of 15 kV, on samples sputter-coated with gold. The distribution of fibre diameters was determined through the measurement of about 250 fibres by means of an acquisition and image analysis software (EDAX Genesis), and the results were given as the average diameter ± standard deviation. Fibre packing density was obtained by means of an image analysis software (Image J). Ten cross-section SEM images were analyzed for each type of electrospun mat and the results were given as mean value and standard deviation of the percentage ratio “black area/white area”.

Results and discussion

In this work, we design smart electrospinning collectors, composed of a steel sheet coated with an enamel layer, in order to obtain electrical resistivity values intermediate between those of semiconductors and good insulators. Collector resistance is modulated by playing on the enamel layer thickness, while keeping constant the enamel chemical composition.

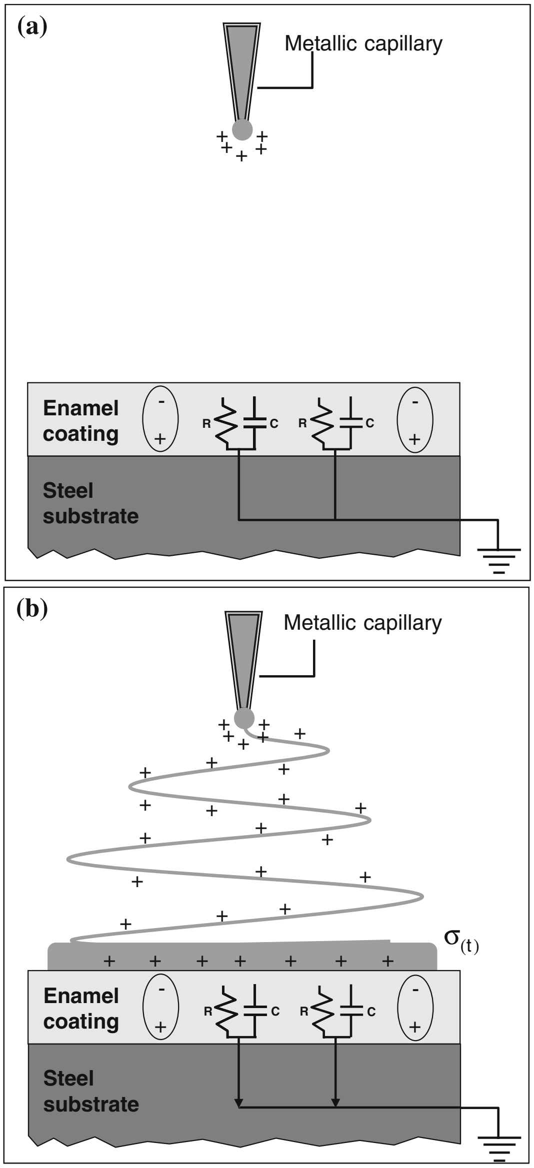

Fig. 1 Schematic illustration of the electrostatic phenomena occurring during the electrospinning process using enameled collectors. **a** Starting situation before fibre deposition and **b** after deposition of a layer of polymer fibres

In order to explain the mechanism governing the action of the innovative electrospinning collectors, Fig. 1 sketches the electrostatic phenomena occurring during the electrospinning process in the presence of the enamelled steel collectors. When a positive high voltage difference is applied between the metallic capillary ejecting the polymeric solution and the grounded counter-electrode acting as the nanofibre collector, the enamel dielectric layer is subjected to polarization. Therefore, charges of opposite sign with respect to that of the source electrode are formed within the vitreous matrix (Fig. 1a). At the same time, the positively charged polymer solution is ejected in the form of a thin fluid jet travelling towards the grounded target. As soon as fibres reach the collector, they tend to rapidly discharge. However, when a uniform layer of fibres is deposited (Fig. 1b), fibre discharging becomes less efficient and the collector surface acquires a positive charge density (σ) that decreases with time due to charge relaxation process of the enamel coating. This phenomenon depends upon the electrical properties (resistance, R and capacitance, C) of the enamelled electrode. A simple R–C circuit can be used to describe the charge relaxation process, where the surface charge density exponentially decays with time according to the following equation:

$$\sigma(t) = \sigma_0 \exp\left(-\frac{t}{\tau}\right) \tag{1}$$

where σ_0 is the surface charge density at time $t = 0$ s and τ, the time constant of charge relaxation process, is the product of electrical resistance and capacitance of the enamelled specimen. The electric field generated by σ, $E_\sigma(t)$, is perpendicular to the surface and, at a given time t, it depends only on $\sigma(t)$. For a planar uniform surface charge distribution, $E_\sigma(t)$ is provided by:

$$E_\sigma(t) = \frac{\sigma(t)}{2\varepsilon_0} \tag{2}$$

where ε_0 is the vacuum dielectric constant.

The electric field $E_\sigma(t)$ counteracts the external applied field and it generates a repulsive force acting on the incoming positively charged fibres. This fibre repulsion effect depends on the discharging rate of the fibres at the collector (Eq. 1), which is associated with the resistivity of the enamelled target. The longer the charge relaxation time constant, the higher the positive charge accumulation at the enamel surface at a given time, $\sigma(t)$, thus a higher repulsive force is generated.

The electrical properties of a first series of collectors (Type A) with different enamel thickness were characterized, and results are reported in Fig. 2. The electrical resistance and the electrical time constant ($\tau = RC$) of the enamelled collectors is found to increase with enamel coating thickness (Fig. 2), in agreement with previously reported results [32]. The electrical properties of the collectors play a critical role in the electrospinning process, as will be shown hereafter.

The above described enamelled collectors are used to fabricate electrospun mats of poly(L)lactic acid. Fibre diameter distribution (650 ± 200 nm) is not affected by the type of collector used. On the contrary, fibre packing density is found to depend on enamel thickness, as can be visually appreciated by the SEM images of polymeric mat sections reported in Fig. 2. Fibre packing density is also estimated from the ratio "black area/white area" in the cross-section SEM images. Values of (24 ± 4), (30 ± 5) and (43 ± 6)% are obtained when fibres are collected on steel, on a 0.15-mm thick enamel coating and on a 0.53-mm thick enamel coating, respectively. By increasing enamel layer thickness, mat porosity is enhanced due to slower charge dissipation that causes higher repulsive electrostatic forces on the incoming charged fibres. These results demonstrate that mat porosity can be easily modulated by changing the electrical resistance of the enamelled

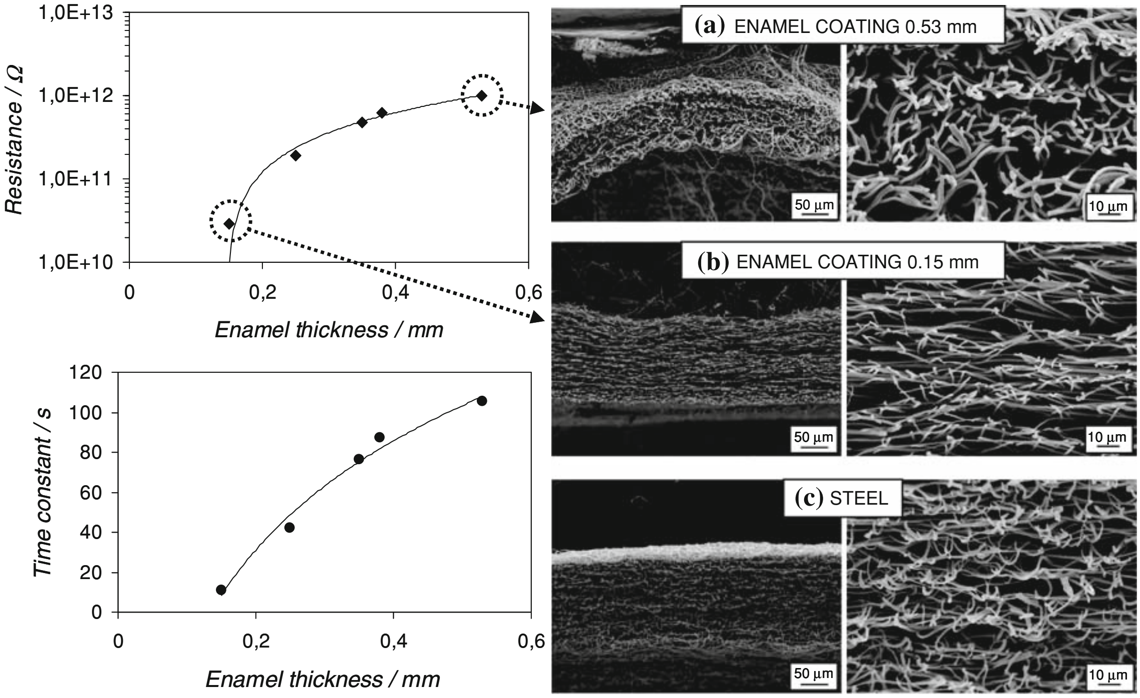

Fig. 2 *Left*: electrical resistance and time constant of Type A enamelled collectors as a function of enamel coating thickness. *Right*: SEM micrographs (two different magnifications) of electrospun mat sections obtained from collectors with different enamel thickness: **a** 0.53 mm; **b** 0.15 mm and **c** steel collector

electrode through a suitable selection of the enamel layer thickness.

The electrical properties of the new enamelled collectors herein presented, can be modified by doping the bulk enamel with proper additives, with the aim of affecting the electrostatic charge diffusion and charge distribution on the collector during the electrospinning process. When montmorillonite clay particles are randomly distributed in the vitreous matrix, a star-shaped pattern is observed on the electrospun polymer mat deposited on this modified enamelled collector (Type B) (Fig. 3a). This result demonstrates that such modification of enamel composition is able to influence fibres deposition during mat fabrication. This finding might be associated with the high electrical mobility of the alkaline metals ions present in the montmorillonite clay, which locally decreases electrical resistivity of enamels. Indeed, when conductive additives are inserted within the enamel coating, the relaxation time constant becomes non-uniform all over the collector surface and, according to Eq. 1, the more conductive areas of the surface possess a lower charge density. This means that the force generated by the electric repulsive field is lower close to the more conductive particles (Eq. 2), that act as 'potential wells' and aggregation centres for the incoming nanofibres, thus leading to a star-shaped fibre deposition (Fig. 3a).

It is noteworthy that relative humidity (RH) of the environment influences the degree of orientation and fibre patterning. In particular, a lower orientation degree is obtained with an increase of RH. This phenomenon is easily explained considering that air water molecules promote fibre discharging and, as a consequence, the orientation effect due to electrostatic repulsion becomes less effective. This evidence strengthens the concept that repulsive charge density at the collector plays a key role in fibre patterning.

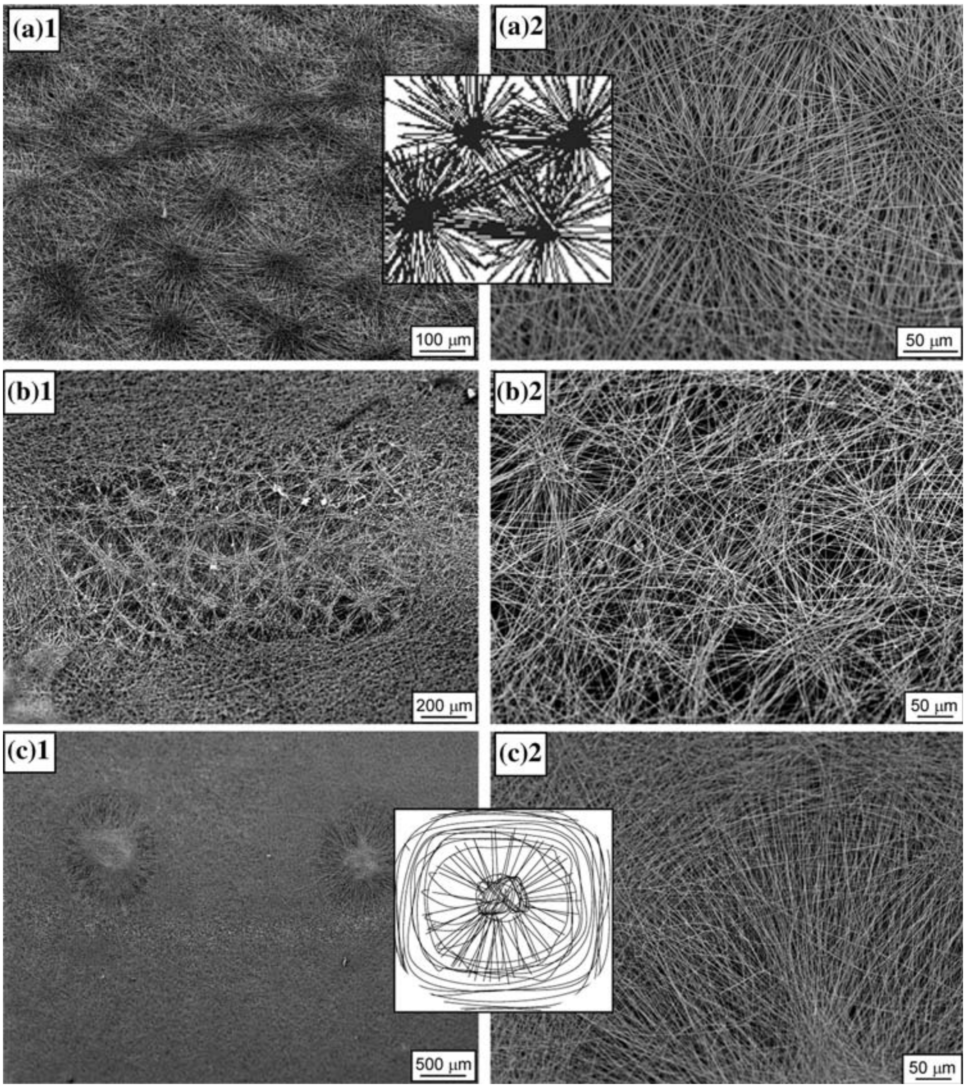

Fig. 3 SEM images (two different magnifications) of: **a** star-patterned electrospun mats from Type B collector containing montmorillonite clay particles; **b** electrospun mats from Type C collector locally doped with micrometric alumina; **c** electrospun mats from Type C collector modified with points of serigraphic paste. The *insets* show a sketch of fibres pattern

Additional patterns in electrospun nanofibrous mats can be obtained by suitable local doping of enamel surface. As an example, the enamel surface is modified by inserting in a small rectangular area, micrometric alumina particles (Type C collector). Again, such collector modification generates a star-shaped pattern localized in correspondence to the modified region of the enamel (Fig. 3b). In this case, alumina particles act as points with higher conductivity with respect to the surrounding enamel similarly to montmorillonite particles in Type B collectors.

Another enamel surface modification was realized through application of a graphitic paste forming 'islands' that change both the roughness and the resistivity of the grounded enamelled plate (Type D collector). The pattern of Fig. 3c is obtained, wherein there is accumulation of fibres with random distribution on both the conducting point (graphitic paste) and the enamel. In the confined region around the graphitic point, a low density of fibres is deposited with a radial distribution. As the conductive point is slightly raised with respect to the enamel coating, the observed pattern can be related to the formation of an air gap, having high resistivity between the graphitic point and the enamel coating during fibre deposition. It is reasonable to assume that fibres lying on the air gap remain charged for long time, thus generating a high repulsive force on the incoming fibres. A radial fibre pattern with a ring of parallel fibres around the charged circular zone is therefore obtained (Fig. 3c).

Results of this work demonstrate that electrospun mats with different patterned architectures can be obtained by properly designing the collectors. Nanofibrous materials with patterned microstructures may possess specific properties useful for all those applications requiring materials with suited fibre anisotropy such as, for example, microelectronics, optical and photonic devices, as well as tissue engineering. In the latter field, the possibility to obtain nanofibrous scaffolds with defined microstructures could be advantageous, as it is known that substrate architecture and pattern influence biological responses, such as cell attachment and proliferation, in tissue regeneration. Indeed, the effect of electrospun fibre orientation on cell behaviour is the focus of extensive researches. As an example, in myocardial tissue engineering fibre anisotropy was found to greatly modulate engineered cardiac tissue structure and function [33].

Conclusions

This work proposes a novel, simple and versatile way to fabricate nanofibrous mats with desired patterns and porosity by acting on the material constituting the collector, in particular, on electrical charge distribution and charge diffusion on the collector itself. Enamelled collectors are low cost materials that, compared to classical metal collectors, possess many advantages, such as tunable electrical conductivity, low roughness, good cleanability, resistance to corrosive agents and chemical solvents, wear and abrasion resistance. Moreover, they should offer a non-sticking surface to almost all electrospun polymeric materials. The possibility to modify enamel surface through serigraphic or lithographic techniques will enable production of smart patterned electrospun mats with fibre distribution suitable for advanced applications such as microelectronics, optical and photonic devices, as well as scaffolds for tissue engineering.

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