

Self-Organization of Functional Materials in Confinement

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CONSPECTUS: This Account aims to describe our experience in the use of patterning techniques for addressing the self-organization processes of materials into spatially confined regions on technologically relevant surfaces. Functional properties of materials depend on their chemical structure, their assembly, and spatial distribution at the solid



state; the combination of these factors determines their properties and their technological applications. In fact, by controlling the assembly processes and the spatial distribution of the resulting structures, functional materials can be guided to technological and specific applications. We considered the principal self-organizing processes, such as crystallization, dewetting and phase segregation. Usually, these phenomena produce defective molecular films, compromising their use in many technological applications. This issue can be overcome by using patterning techniques, which induce molecules to self-organize into welldefined patterned structures, by means of spatial confinement. In particular, we focus our attention on the confinement effect achieved by stamp-assisted deposition for controlling size, density, and positions of material assemblies, giving them new chemical/physical functionalities. We review the methods and principles of the stamp-assisted spatial confinement and we discuss how they can be advantageously exploited to control crystalline order/orientation, dewetting phenomena, and spontaneous phase segregation. Moreover, we highlight how physical/chemical properties of soluble functional materials can be driven in constructive ways, by integrating them into operating technological devices.

1. INTRODUCTION

Chemical and physical properties of the functional materials depend on their chemical structure, their assembly, and spatial distribution in the solid state; the combination of these factors determines their properties and their technological applications. In fact, by controlling the assembly processes and the spatial distribution of the resulting structures, functional materials can be guided to technological and specific applications. 1,2

Spontaneous organization processes, i.e., self-organization, of materials on surfaces are driven by the balance between intermolecular and molecule-surface interactions, which are the consequence of noncovalent interaction, such as hydrogen bonds, dispersion forces, and steric effects. Material selforganization on surfaces can be addressed by acting on both the rational design of the molecules that constitute the material and the surfaces. However, when self-organizing materials from a solution are deposited on a surface, capillary flows tend to hamper the precise control over the size, shape, and position of the individual structures across large areas, resulting in inhomogeneity that prevents many technological applications that require homogeneous thin films.

Spatial confinement allows us to overcome this problem by controlling the self-organizing phenomena of functional materials, such as (i) self-assembly, i.e., the autonomous organization of components into patterns or structures without external intervention; (ii) crystallization, i.e., the natural process of the formation of solid crystals from a solution or a melt phase; (iii) dewetting, i.e., the rupture of a liquid, or solid, thin film on a surface into an ensemble of separated objects; and (iv) phase segregation, i.e., the local enrichment of a component on the surface (or an internal interface) of a material in a mixture made of two or more materials.

Many strategies have been proposed to spatially confine the self-organization processes including patterning techniques that have been extensively used for organizing materials in specific patterns on surfaces, introducing a new route for achieving material properties suitable for technological applications where continuous films are unnecessary.3

This Account aims to describe, following our experience, the use of patterning techniques for addressing the self-organization processes of materials into spatially confined regions. In particular, we focus on the confinement effect achieved by using micro- and nanostructured stamps for controlling size, density, and the positions of material assemblies, giving them, in some cases, novel functionalities. We review the methods and principles of the stamp-assisted spatial confinement and how they can be used to control self-organization phenomena of functional materials. Moreover, we highlight how physical/ chemical properties of soluble functional materials can be guided in constructive ways by integrating them into operating technological devices.

2. METHODS AND PRINCIPLES OF STAMP-ASSISTED CONFINEMENT

2.1. Stamp-Assisted Techniques

Stamp-assisted techniques have been shown to be a versatile and technologically attractive route for the micro- and

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nanopatterning of a broad range of functional materials such as organic semiconductors, 4-8 coordination compounds, 9-12 magnetic precursors, 13 proteins, 14 DNA, 15 cells, 16 and colloids. 17 The use of a stamp to control the deposition process of soluble materials on substrates is a useful strategy to exploit their self-organization properties in confinement, which in turn could improve their functional properties. In stampassisted deposition a solution is deposited into a region defined by the stamp motif in which self-assembly processes take place. The overall result of the patterning is determined by (i) intrinsic self-organization properties of the material, (ii) interaction between solute and stamp/substrate; (iii) solvent nature, (iv) concentration of the solution, and (iv) size and shape of the stamp features.

Among all stamp-assisted techniques, we briefly describe those that, by our experience, are the most versatile and efficient to confine the deposition of functional materials; microcontact printing (μ CP), micromolding in capillaries (MIMIC), and lithographically controlled wetting (LCW).

2.1.1. Microcontact Printing. μ CP is the most important soft lithographic technique for molecular printing introduced by Kumar and Whitesides in 1993. In μ CP an elastomeric stamp, usually made of poly(dimethylsiloxane) (PDMS), is used to print by contact inks (molecules) capable of forming self-assembled monolayers (SAMs) from the stamp to a surface (Figure 1a). The SAMs form in the zones where the stamp

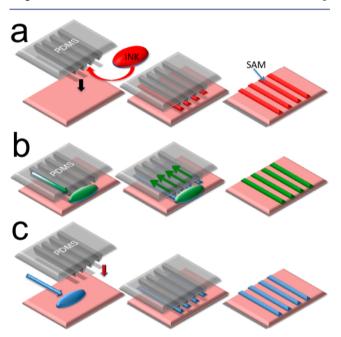


Figure 1. Scheme of principal methods used for deposition in confinement: (a) microcontact printing (μ CP); (b) micromolding in capillaries (MIMIC); (c) lithographically controlled wetting (LCW). Details are reported in references cited in the text.

reliefs go in contact with the surface. Noteworthy, in μ CP the SAM formation is much faster than by conventional or electrochemically assisted procedures ^{19,20} (a few seconds). μ CP has been applied in a wide range of systems, including microelectronics, surface chemistry, and biomaterials. ²¹

2.1.1. Micromolding in Capillaries. MIMIC is a simple soft-lithographic method introduced by Whitesides et al. in 1995.²² It is suitable for fabricating interconnected microstructures on both planar and curved surfaces. In MIMIC

(Figure 1b) an elastomeric stamp (usually made of PDMS) is placed in conformal contact with a surface so that its relief structure forms a network of channels.

If a solution is poured at the open end of the channels, in order to minimize the free energies of the solid—vapor and solid—liquid interfaces (imbibition), the solution fills spontaneously the channels. After filling the channels and a post-treatment, i.e., thermal annealing, UV-radiation curing, or simply a solvent evaporation, the stamp is removed, and a network of functional material remains on the surface.

The main limitations of MIMIC are due to the need for a hydraulically connected network of capillaries, which hampers the formation of isolated structures, and to the limited solvent compatibility of the stamps.²³

2.1.2. Lithographically Controlled Wetting. LCW is an unconventional lithographic method for nanostructuration of soluble functional materials, introduced in 2003 by our group. ^{24,25} In LCW (Figure 1c) a stamp is gently placed in contact with a liquid thin film spread on a substrate, the fluid layer develops instability where the capillary forces pin the solution to the stamp protrusions, forming an array of menisci, which follow the shape of the stamp.

As the critical concentration is reached by solvent evaporation, the solute precipitates onto the substrate inside the menisci, giving rise to a structured thin film that replicates the stamp protrusion. A remarkable outcome of LCW is the possibility to downsize the printed feature size with respect to the lateral size of the stamp protrusions using the appropriate solute concentration^{24,26} taking advantage from the so-called coffee-ring effect²⁷ and the possibility to manipulate the materials self-organization.^{28–30} A detailed protocol of LCW is available in ref 31.

Noteworthy, LCW is a complementary technique to MIMIC since stamps do not require a connected network of capillaries, allowing one to pattern isolated structures, and can be composed of soft but also of rigid materials (i.e., metals, ceramics, and silicon), making LCW adaptable to stringent conditions, such as the use of highly volatile, ²⁴ aggressive, or corrosive solvents, ³² high temperature, ² and magnetic ³³ and electrified surfaces.

3. CRYSTALLIZATION IN CONFINEMENT

3.1. Crystalline Order Improvement and Orientation Control

Molecular crystals are stable aggregates where molecules are arranged in an ordered pattern held together by the van der Waals forces, extending in all three spatial dimensions. Many of the physical properties of materials, such as charge transport, are strongly affected by the molecular arrangement; therefore the control of the quality of the crystals and their positioning are primary issues for the exploitation of the functional properties in many technological applications.³

The crystallization is governed by intertwined thermodynamic and kinetic factors, such as molecular diffusion, solute—solute, solute—solvent, and solute—substrate interactions, and shrinking rate, which can make the crystallization highly variable and difficult to control.³⁶

The crystallization process from a solution starts with the nucleation step, where the molecules of the solute dispersed in the solvent reach supersaturation and start to gather into stable clusters (i.e., nuclei), and proceeds with the growth of the nuclei (crystal growth step).

Spatial confinement of the crystallization process implies both the decrease of the evaporation rate of solvents, increasing the mean size of crystalline domains (due to the decreasing of the number of nuclei), and limits the molecular diffusion, increasing the energy available for molecular motions during the crystallization, therefore optimizing the process.

The critical role of the confinement of the crystallization process on the orientation of the crystallites and on the functional properties has been shown on a wide range of functional materials, such as spin-crossover (SCO) compounds and organic semiconductors (OS).

A representative example was reported using one-dimensional SCO compounds applying LCW, 11,37 using stamps consisting of parallel lines. Stripes of randomly sub-micrometric crystallites were formed with a crystallization time reduced by 1 order of magnitude, with respect to the drop-cast film, preserving the SCO properties that critically depend on the molecular environment (e.g., packing, crystallinity, type of solvent, and ionic strength, etc.).

By reducing the spatial confinement dimension from 1 μ m to 200 nm, highly oriented crystalline structures with a resolution of approximately 160 nm are formed (Figure 2).³⁷ The

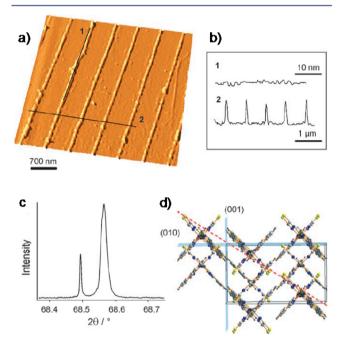


Figure 2. (a) Atomic force microscopy (AFM) topography of nanostripes of *cis*-bis(thiocyanato)bis(1,10-phenanthroline)iron(II) fabricated by LCW on silicon. (b) Line profile (1) and cross-section (2) corresponding to the features labeled in panel a. (c) GIXD azimuthal scan for (010). (d) Top view of the 3D structure of the compound in the nanostripes oriented along the red line. Reprinted with permission from ref 37. Copyright 2008 Wiley-VCH Verlag GmbH and Co. KGaA.

anisotropic spatial confinement leads to a preferred orientation of the crystallites, where a particular crystallographic direction coincides with the direction of the parallel lines of the stamp, as confirmed by azimuthal scans of an in-plane Bragg reflection in grazing geometry (Figure 2c). Two peaks, a few hundredths of a degree apart, are associated with a double population of crystallites, that is, a high amount of small crystallites (the strong and broad peak) and a smaller amount of larger crystallites (the weak and sharp peak), oriented as depicted in

Figure 2d. In this case, the appearance of crystallinity in well-oriented nanostructures is a breakthrough, ¹² since molecular SCO properties critically depend on the uniformity of the local environment around the SCO switching units. ³⁸

Molecular order is also fundamental in organic electronics, since charge transport properties of the organic semiconductors strongly depend on both the degree of crystallinity and the direction of $\pi-\pi$ interactions between the conjugated molecules with respect to the applied voltage. For instance, in organic field effect transistors (OFETs) the charge carriers flow along the channel between source and drain electrodes and their mobility is maximized when the $\pi-\pi$ stacking is parallel to the film plane.

LCW has been proven to be a powerful technique to fabricate OFET in which charges flow through a defined array of nanostripes, 100-200 nm wide and a few monolayers high, made of crystalline and highly ordered domains, where $\pi-\pi$ stacking is oriented along a unique direction parallel to the film plane. As a consequence of the increased crystallinity, OFETs based on nanostripes have shown charge mobility 2 orders of magnitude higher than OFETs based on spin-coated thin films.

Crystalline nanostripes of organic semiconductors were also used as a building block for ambipolar devices. The first successful attempt was the fabrication of stripes based on n-type perylene-based semiconductor with the subsequent deposition of a pentacene (p-type) ultrathin film.⁵ Deposition in confinement has induced the molecules to form crystals with the π - π stacking oriented parallel to the surface, leading the stripes-based FETs to exhibit a charge mobility 2 orders of magnitude higher than that obtained for films grown by drop casting or spin coating, where crystals are randomly oriented. The crystallinity of microstripes remains stable after depositing pentacene, providing the optimal configuration for the charge transport in the ambipolar planar transistor. Moving from micro- to nanoscale confinement, self-assembly changes from textured to one-dimensional oriented crystalline structures. However, depending on the solvent and ambient conditions, highly crystalline and oriented stripes can be also obtained at the microscale. When molecules have the ability to selfassemble into thermodynamically stable nano- and microsized fibers, the deposition in microchannel allows us to align such fibers along a unique crystallographic direction, as we recently reported using thiophene octamers (Figure 3a).³⁹ On the other hand, when the same compounds are drop-cast on a substrate, molecules arrange in randomly distributed fibers (Figure 3b) which produce a diffraction pattern containing a large number of peaks which are invariant upon rotation of the sample around its normal. 2D-GIXD images of aligned fibers fabricated by LCW reveal different reflections when the X-ray beam is parallel or perpendicular to the fiber direction (Figure 3c,d). This strong anisotropy in the reflections indicates that the alignment of the fibers involves an anisotropic distribution of their molecular organization, as proposed in Figure 3e.

Deposition in confinement also improves the crystallization process of polymeric materials. Polymers are semicrystalline materials with low long-range order. When polymers are completely amorphous, they are thermally annealed to improve crystallinity. For instance, the diketopyrrolopyrrole-benzothia-diazole-based copolymer (PDPP-TBT) has revealed exceptional ambipolar properties only after thermal annealing. As expected for this kind of polymers, spin-coated films are characterized by an amorphous structure, as indicated by the lack of diffraction peaks in the 2D-GIXD image (Figure 4a).

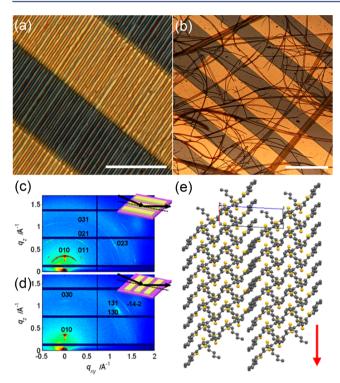


Figure 3. Optical micrographs (a) of aligned (scale bar = $20~\mu m$) and (b) randomly distributed (scale bar = $50~\mu m$) fibers on an interdigitated gold electrode/SiO₂ surface. 2D-GIXD images of aligned fibers recorded with the X-ray beam (c) parallel and (d) perpendicular to their direction. (e) Schematic illustration of the molecular organization of oligothiophene along the fiber direction (red arrow). Reproduced with permission from ref 39. Copyright 2012 The Royal Society of Chemistry.

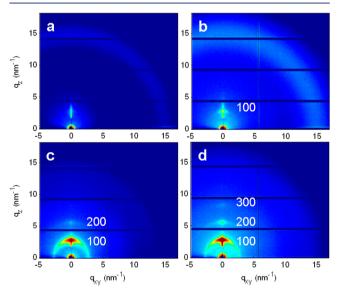


Figure 4. 2D-GIXRD images collected for PDPP-TBT films prepared by spin coating (a, b) and LCW (c, d) before and after annealing at $200\,^{\circ}$ C, respectively. Reprinted with permission from ref 6. Copyright 2013 American Chemical Society.

After thermal annealing, the lamellar (100) Bragg peak (Figure 4b) appears in the 2D diffraction pattern, indicating the edge-on configuration. Microstripes printed by LCW exhibit lamellar reflections into the 2D-GIXD images (Figure 4c,d) without any annealing treatment.

The effect of confinement on the crystallization process was also used in other complex systems to enhance the quality of crystals, such as precursors of metal—organic-framework 40 and functional polymers 30,41,42

3.2. Local Orientation in Liquid Crystals

The effects of crystallization in confinement are not limited to the materials at the solid state. An illustrative example is offered by discotic liquid crystals (DLCs) that are a class of material that spontaneously assembly in columnar superstructures formed by stacking of disk-like molecules. When deposited onto a surface, regardless of the nature of the substrate, the columns spontaneously orient parallel to the surfaces (edge-on phase) and exhibit a high birefringence. If the so achieved DLC film is confined between two surfaces and treated by a heating and cooling process at isotropic transition temperature ($T_{\rm I}$), the columns reorient perpendicular to the surfaces, forming the sonamed homeotropic phase, which has a very poor birefringence.

Recently, our group demonstrated that, using the spatial confinement, it is also possible to locally modify the alignment of DLC columns in the film.² Figure 5a shows the scheme of

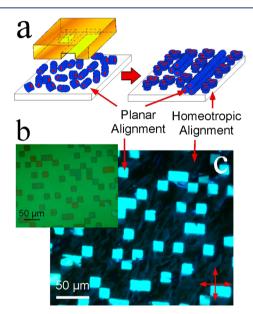


Figure 5. Stamp-assisted melting and quenching at $T_{\rm I}$ of DLC induces a spatially controlled columns orientation in continuous thin films: (a) Scheme of the process. (b) optical micrographs in bright field of the stamp, and (c) with cross-polars of the patterned DLC film. Reprinted with permission from ref 2. Copyright 2009 Wiley-VCH Verlag GmbH and Co. KGaA.

the process and the results of patterning. As a microstructured stamp with recesses and protrusions is placed on a film of DLC without applying an external pressure and the system is brought to a temperature $T > T_{\rm I}$ for a few seconds, the columns in correspondence of recesses retain their original planar alignment, while in correspondence of the stamp protrusions, where the film is locally confined, the columns are reoriented to the homeotropic alignment. Therefore, the process allows us to produce specific column orientation at preselected regions of a DLC film.

4. DEWETTING IN CONFINEMENT

Dewetting is a spontaneous phenomenon where a thin film on a surface ruptures into an ensemble of separated objects. It occurs when the film is metastable or unstable (e.g., the spreading coefficient < 0) and can be triggered by local defects present on the surface or due to collective fluctuations (spinodal dewetting)⁴⁴ or can be induced (and confined) by an external stimulation.

Dewetting leads to spontaneous patterning with spatial correlations; however, a precise control of the individual structures is very difficult. Precise positioning and size control of the dewetted structures are possible by confining dewetting phenomena. Confinement enhances the effect of spatial correlation driving the distribution of droplets toward an ordered system. 45,46 Confined dewetting has been exploited in many technological applications⁴⁷ that include several materials ranging from single molecule magnets²⁵ to supramolecules^{48,49} and biomolecules.¹⁵ Another efficient approach is the triggering of dewetting by external stimuli that can be spatially controlled such as a mechanical perturbation imposed by an AFM tip. 45,46 In this case the external perturbation imposes a spatial constraint that introduces its own length scales in superposition with the spontaneous length scales of the dewetting process. The result is the enhancement of long-range spatial correlations of the dewetted structures. Ordered nanostructures were obtained by confining dewetting into the zones scanned by AFM in contact mode obtaining a parallel array of nanostripes in case of 2D confinement and an ordered distribution of dots by 1D confinement (e.g., along a single scan line of AFM) using a thin film of rotaxanes. Figure 6 shows the effect of 2D and 1D confinement of dewetting, where a regular distribution of nanostripes and nanodroplets is obtained by 2D and 1D confinement. The system was successfully used for high-density information storage. ⁴⁵ The process requires the thin film reorganization via dewetting and a relatively low energy barrier of activation; therefore, a limited number of systems can be reorganized by this technique.

5. PHASE SEGREGATION IN CONFINEMENT

Phase segregation (PS) is a spontaneous process, which occurs in binary blend, whose driving force is the different surface energy between the components. In thin films, PS generates two (or more) phases made of blend components. PS can be spontaneous or induced by thermal or solvent stimulation. While PS gives rise to a random distribution of different phases, the situation changes in confinement. In 2005 our group developed a new process combining PS and micro-transfer molding using a blend made of Mn₁₂-based molecular magnets and polycarbonate, which is a system that segregates upon solvent annealing. ⁵⁰

When this Å blend structured by protrusions and recesses is exposed to solvent vapors, it swells reducing the glass-transition temperature below room temperature. Upon these conditions, the protrusions are smooth due to the effect of the surface tension, reducing their surface area. The smoothing occurs at the same time of the PS; therefore the segregating molecules concentrate in these zones transforming the topographic pattern into a chemical pattern. Figure 7a shows a scheme of the process.

Moreover a longer solvent annealing treatment induces a further reorganization on the segregate phase forming a regular

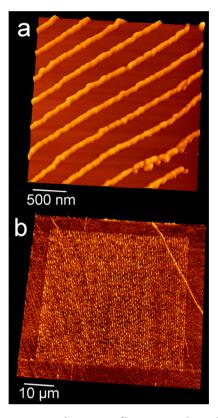


Figure 6. Patterning of rotaxane films on graphite obtained by dewetting in confinement triggered by mechanical perturbation performed by an AFM tip in (a) two dimensions and(b) one dimension. Adapted with permission from ref 46. Copyright 2006, National Academy of Sciences.

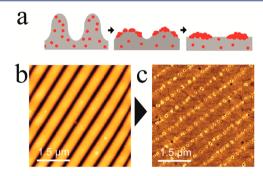


Figure 7. (a) Scheme of lithographic controlled PS. (b) Molded film of SMM dispersed in polycarbonate. (c) Ordered patterning of SMM O-ring obtained using method reported in panel a. Reprinted with permission from ref 51. Copyright 2006 American Chemical Society.

distribution of O-ring on the surface of the polymer (Figure 7c). 51

6. CONFINEMENT OF BIOLOGICAL SYSTEMS

Biological molecules are probably the most complex objects to be handled by fabrication techniques. This is due mainly to the requirement of preserving during all the fabrication steps their structure and their biological function. The structure of biological molecules is in fact determined by several different types of noncovalent interactions such as hydrogen bond, hydrophobic interaction, and ionic interaction. The organisms finely tune their 3D assessment of these interactions according to the environment, where these molecules should carry on

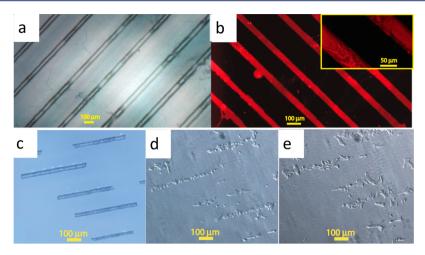


Figure 8. Example of patterning of biological material. Laminin patterns onto Teflon-AF are fabricated by LCW (a) and remain stable for 24 h under cell culture conditions (b). Neuroblastoma cells cultured onto a segment pattern (c) selectively adhere (d) and reach confluence at 48 h only on the patterned laminin segments. Reprinted with permission from ref 16. Copyright 2010 Wiley-VCH Verlag GmbH and Co. KGaA.

their activity: in contact or embedded within membranes or in bulk solution at different ionic strength.

The environment faced in vivo by protein and nucleic acids is anyway always rather crowded; therefore, their activity is mostly performed in close contact with other molecules.

The most remarkable example is the extremely high confinement that takes place within the cell nuclei or in the virus capsids where both proteins and nucleic acids are confined in very small spaces. The described situation can represent a bottleneck for fabrication because in any step of this process the proteins or nucleic acids would be in a condition far from their ideal ones. However, these objects are suitable for being under strong confinement, and this can represent a strategy for many fabrication approaches.

MIMICs and LCW have been used in this frame because in both of them the menisci withdrawing due to the solvent evaporation lead to droplets where the solute concentration reach very high values that can drive important phenomena.

A representative example is the patterning of Laminin on an antifouling surface such as Teflon-AF. 16 Laminin is a protein of the basal lamina playing a central role in cell adhesion, migration, and proliferation; it acts as a bridge between the extracellular collagen fibers and the cell adhesion points. Laminin when confined can form compact self-assembled layers, and thus, using LCW, we were able to form controlled patterns of laminin on a Teflon surface; the most remarkable properties of the fabricated features is that they are stably adsorbed on an antifouling surface even when exposed to the conditions of cell cultures. It means that upon rehydrating in cell culture media, at 37 °C for several days the features do not dissolve and the locally positioned proteins preserve their structure. In Figure 8, it is reported one of the patterns achieved and, beside the optical image obtained just upon fabrication, an immunofluorescence assays is displayed where it can be noted how, upon 1 day of incubation under cell culture conditions, the pattern remains stable and well-localized. The adhesion of cells is also reported to show how such a confinement-based fabrication technique can produce important results as the selective positioning of cells on a surface where normally no cells would attach.

Similar results have been obtained by MIMIC using proteins and nucleic acids. In this case the balance between the diffusion of the molecules in the highly confined and crowded

environment and their adsorption onto the surface has allowed design of a complex pattern as multiple protein gradients¹⁴ and DNA nanodots.¹⁵ In Figure 8 are reported two examples of these application.

7. CONCLUDING REMARKS

In this Account, we have discussed self-organization in confinement and its possible exploitation as a novel fabrication tool. We have shown that deposition in confinement can be effectively used to enhance self-organizing properties of many functional materials. Deposition in confinement allows us the patterning of the material into defined zones that can be effectively used for the fabrication of small and regularly spaced addressable and homogeneous functional nanostructures. Confinement provides an improvement of properties such as the crystallinity, allowing, in some cases, the control of crystal orientation. These improved properties can be directly exploited in technological application since they affect the performance of corresponding devices and extend the potentialities of materials toward new applications. It is a matter of fact that deposition in confinement is the basis of several bottom-up nanofabrication methods³² because it offers direct advantages in applications where inhomogeneous functional thin deposits would not be applicable. Further challenges include the application of confined deposition in emerging fields as the manipulation and control of polymorphism⁵² toward technological application in traditional and new devices.

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Notes

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Francesco Valle received a Master's degree in Physics from the University of Roma "La Sapienza" in 1999 and the Ph.D. in Science from the University of Lausanne, Switzerland. He is a Research Scientist at CNR-ISMN Bologna from 2009. His research interests include polymer physics, single-molecule techniques, protein folding, and cell adhesion.

Cristiano Albonetti, Physicist. He took his degree in Physics at Bologna University in 2000 and Ph.D. in Physics in 2005. He has worked at the ISMN-CNR since 2001. Its research activities are focused on scanning probe microscopies (SPMs), implementation and development of new SPM techniques, ultrahigh-vacuum systems, growth of organic and inorganic materials, and surfaces nanostructuring.

Fabiola Liscio, postdoctoral fellow at CNR-IMM Bologna. She got laurea in Physics cum Laude in January 2005 at "Roma Tre" University (IT) and she received a Ph.D. Physics/Material Science in January 2009 at SIMaP-INPG in Grenoble (France). Her current research interests are focused on the study of organic—organic and organic—inorganic interfaces by means of X-ray scattering techniques.

Massimiliano Cavallini has a Ph.D. in Chemical Science and was a EURYI Awardee in 2006. Cavallini is senior researcher at CNR-ISMN Bologna since 2000, working in the interdisciplinary field of nanotechnology. He is author of more than 100 papers in highly qualified peer-reviewed international journals and 14 international patents. He has been Principal Investigator and coordinator of several EU and National Projects.

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