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# Bottom-Up Assembly of Micro/Nanostructures

Massimo Mastrangeli\* and Michele Perego\*

Putting order into matter has been a key human enterprise since millennia. Sculpting or assembling components into shapes suitable for solving tasks has significantly expanded the reach of human actions, adapted the landscape wherein those actions took place, and modified human behaviour. Technology has thus arisen and progressively evolved in time to develop production tools and inspection instruments that cooperated to address ever more needs and enable ever more functionalities, some only possible in synthetic form. This ongoing process has witnessed a strong acceleration in the last century by aiming in particular at miniaturization and manipulation of micro- and nanoscopic objects. This push was largely fuelled and in turn rewarded by the unprecedented computational and commercial success that micro/nanoelectronics could achieve by aspiring to demonstrate the functionality of ever smaller feature sizes and consequently faster devices.<sup>[1]</sup>

As Feynman foresaw some 60 years ago,<sup>[2]</sup> lots of opportunities for deeper knowledge and disruptive technology have emerged from imposing order to matter at micro- and nanoscale. The latter effort continues to pose fantastic challenges to scientists and engineers: on the one side, this size range is poised at the limits of what top-down information transfer can do to structure matter by means of lithography and additive manufacturing techniques; on the other side, it entails more sophisticated structures than those that can be achieved by the growth of periodic crystals. Nevertheless, and to our formidable advantage, the physics at play in this middle ground is uniquely suitable to inform predictably ordered patterns even without extrinsic intervention.<sup>[3]</sup> The variety of forces and selective interactions of comparable magnitude available at sub-millimeter scale has no comparison to any other size range.<sup>[4]</sup> Concurrently, low-dimensional structures like surfaces, wires and dots manifest properties and capacities that substantially differ from those of bulk materials. By the 90's supramolecular chemistry had demonstrated that precise and controllable organization of matter at nanoscale was possible in such playground also in absence of global information imposed by master planners.<sup>[5]</sup> This momentous lead in turn inspired many scientists to export such bottom-up or self-assembly



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approach to the construction of target structures to much larger scales,<sup>[6]</sup> thereby including the millimetric<sup>[7]</sup> and centimetric.<sup>[8]</sup> It is tempting to roughly quantify the popularity of self-assembly in recent scientific literature by means of a quick archive search by keyword: **Figure 1** evidences a steep and almost constant rise of the number of documents containing “self-assembly” in the last 20 years.

In the wake of the enduring interest and wealth of possibilities empowered by self-assembly, the purpose of this Special Issue was to create a collection of invited contributions that would highlight some of the most recent trends and appealing applications for bottom-up assembly at the micro- and nanoscale. ADAMI offered kind hospitality to our ambition, and we consider the Issue very fitting for the interdisciplinary scope and audience of the journal – at the interface indeed between multiple fields and interests. A quick look at the Table of Contents reveals an emphasis on one of the most studied and versatile self-assembled materials, i.e., block copolymers and their multiple parametric properties, constellated by contributions on tuneable nanoparticle arrays, monolayer doping of nanowires, functionalization of polymer nanoparticle, capillary self-folding, and a glance into macroscopic self-assembly. What follows is a short introduction to each contribution.

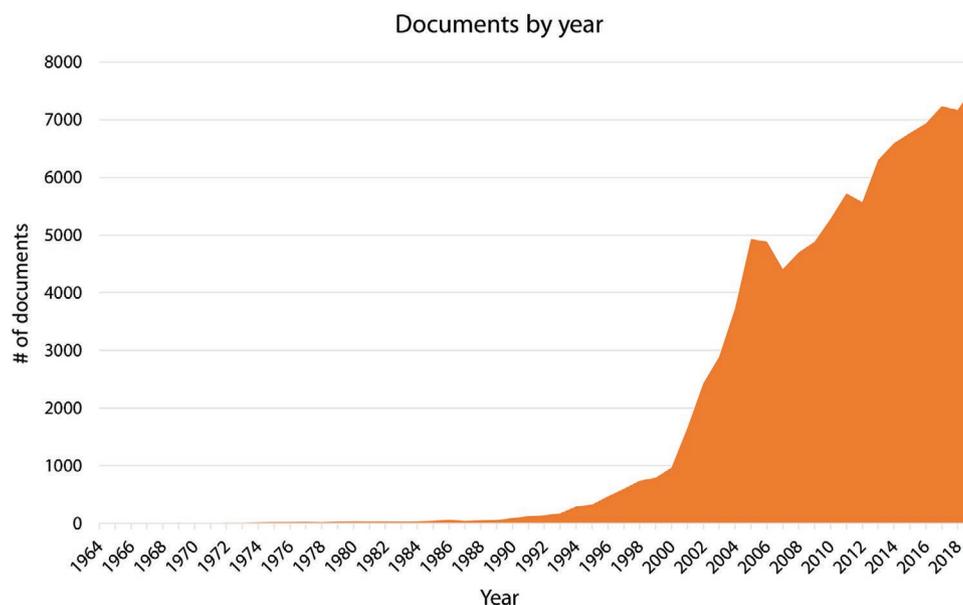
Nanowires are a notable example of nanoscale components whose functionality for, e.g., sensing and optoelectronic applications needs carefully controlled and highly uniform doping profiles. To address this challenge, a viable alternative to in situ doping (i.e., doping during nanowire growth) consists in using molecular monolayers as ex situ and self-limiting dopant sources. Methodologies for monolayer doping are advancing rapidly by virtue of research on improved surface chemistry, capping layers and annealing schedule to control doping levels. These works are accumulating a detailed knowledge of the dynamics of monolayer fragmentation at different stages of the doping process and of their impact on doping levels and uniformity. However, a comprehensive understanding of

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**Figure 1.** Documents containing the keyword “self-assembly” published from 1964 until end of 2019, according to the Scopus database. The grand total amounts to more than 105'000 documents.

monolayer damage due to specific types of surface chemistry, as could be obtained by the application of different monolayer doping methodologies, remains elusive. In this regard, Tzaguy et al. present a detailed study of boron doping of silicon substrates and nanowires, whereby three methodologies developed in Yerushalmi's group are compared to shed light on the molecular decomposition processes at play and their impact on doping.<sup>[9]</sup> In providing guidelines for future developments, the authors demonstrate damage of phenyl boronic acid monolayers by the elevated deposition temperatures of the oxide cap ahead of thermal anneal and activation steps, and suggest that, in specific cases, higher doping levels are attainable without applying the oxide capping.

Klinger et al. review a versatile approach to the synthesis of functional polymer nanoparticles based on post-polymerisation functionalisation of reactive precursor particles.<sup>[10]</sup> Inspired by a similar practice established in the synthesis of linear polymers, this powerful approach offers the advantage of introducing a large variety of functional groups in particle cores and/or surface while safeguarding particle size and size distribution. The authors argue that, though not affording a single, universal strategy that can address all functionalisation needs, post-polymerisation modification provides a synthetic framework to increase functional group tolerance and comparability between differently functionalized particles, which instead remain standing issues for more conventional techniques. In so doing, this approach largely enriches and complements the landscape of colloid functionalization methods, and prompts the formulation of libraries of multifunctional particles. These libraries may represent in turn a significant step to illuminate structure-property relations, and establish universal concepts to instruct colloid synthesis and tailor colloid properties towards innovative applications, such as drug delivery, personal medicine, chemical sensing and catalysis.

Colloidal assembly finds an important application in the fabrication of high-quality structured arrays of nanoparticles for plasmonics. The localized surface plasmon resonances of single nanoparticles typically have broad width and low quality factors. However, ordering a large set of such nanoparticles into a planar array with precise lattice spacing allows the overlap and coherent interaction of the nanoparticles' plasmonic resonances into lattice surface resonances. The ensuing standing waves greatly reduce the spectral linewidth and energy loss of the resonances and enhance energy confinement in sub-diffraction volumes. In their paper, Brasse et al. describe lattice plasmon resonances and the suitability of nanoparticle assembly methods for their fabrication.<sup>[11]</sup> The flexibility afforded by colloidal assembly methods in terms of particle composition (material, shape and size of chemically-synthesized particles) and geometry of achievable structures, together with their simplicity, low cost and low environmental impact as compared to lithography- and etch-based options, do represent significant advantages. The authors review recent progress in colloidal assembly mediated by liquid interfaces and by solid substrates, the latter pre-patterned to work as electro-chemical or topographical templates by a variety of techniques, including microcontact printing, etching, wrinkling or moulding. Brasse et al. highlight the interest of elastomeric substrates for mechano-plasmonic effects such as dynamic tuning of the optical response of nanoparticle arrays by mechanical deformation of the templates, which may open an attractive option for strain sensing, tuneable filters and display technology.

Block copolymers represents an extremely flexible and powerful platform for the synthesis of high-density periodic nanostructures with characteristic dimensions below 100 nm.<sup>[12]</sup> Several studies faced the problem of block copolymer self-assembly, providing novel technological solutions that allowed to control the process in bulk phase or in thin films. The latter option attracted a lot of interested because of the possible

application in advanced lithographic processes for the fabrication of ultra-scaled microelectronic devices.<sup>[13]</sup>

Different approaches have been developed to transfer energy to block copolymer macromolecules promoting phase separation and grain coarsening. Novak et al. focus their review on thermal and photo-thermal approaches that provide access to extreme processing conditions, such as very high temperatures, large heating rates and very sharp thermal gradients.<sup>[14]</sup> As a consequence, photo-thermal methods often achieve vastly improved order using much shorter annealing times compared to conventional annealing in oven or on hot plate, broadening the versatility of block copolymer materials. In particular, photo-thermal zone annealing, which involves the movement of a hot zone through the polymeric film, provides an efficient method to promote high order and facile macroscopic alignment in the block copolymer template.

Similarly, chemical or topographical pre-patterning of the substrate has been demonstrated to provide an efficient tool to achieve the alignment of microdomains in block copolymer templates, and several approaches have been proposed in the literature.<sup>[15]</sup> Brassat et al. explore the possibility to control position and morphology of self-assembled block copolymer thin films on pre-patterned surfaces to generate hierarchical nanostructures.<sup>[16]</sup> Their progress report gives an overview on the interplay between block copolymer film thickness modulation and microphase separation, shedding new light on the role of interfacial energies in both events. In particular, micro-scale processes determining the topography of block copolymer films, i.e., hole/island formation and dewetting into droplets, are presented. Similarly, nanoscale microphase separation into energetically favorable pattern orientations is discussed in relation to polymer film thickness and surface polarities. Finally, the combination of microscale dewetting and nanoscale microphase separation is exploited to create hierarchical nanostructures from block copolymer thin films.

Although block copolymers represent an elegant tool to generate complex periodic patterns with exquisite symmetries, they are somehow limited in terms of attainable geometry in the self-assembled templates. The thermodynamic driving force, generated by the incompatibility between the constituent blocks, determines the specific morphologies that can be achieved during the phase separation, directing the block copolymer toward the formation of well-defined structures by minimizing the interface between the blocks. To overcome this intrinsic limitation, strategies to enrich the variety of structures obtained by block copolymer self-assembly are gaining more and more momentum.

A first strategy aims to create novel three-dimensional nanostructures by iterative layer-by-layer self-assembly of conventional block copolymers generating specific structural motifs and symmetries. In their review, Demazy et al. present an overview of novel iterative block copolymer self-assembly processes stacking different block copolymer layers for the generation of “non-native” morphologies beyond the classical bulk equilibrium phase diagram.<sup>[17]</sup> They highlight the great progress in the design of multilayered hierarchical structures enabled by both the understanding of the mechanisms controlling self-assembly in block copolymer thin film and the development of hybridization methods for the

immobilization of the block copolymer pattern and deposition of an additional block copolymer film. At the same time they identify several challenges, such as those related to the implementation of suitable protocols for the precise registration of the block copolymer features and to the understanding of defect annihilation mechanisms in the formation of such structures.

A second strategy relies on a more fundamental approach based on macromolecular engineering. Different morphologies can be achieved by incorporating additional chemical blocks generating complex molecular architectures and by moving from linear to star, brush, or more intricate copolymers. In their review, Matsushita et al. present different approaches to generate non-conventional morphologies in block copolymer thin films using linear triblock copolymer blends and star block copolymers, i.e., copolymers with different blocks sharing a single common junction.<sup>[18]</sup> They also report data about new self-assembled structures in blends of block copolymers introducing intermolecular associations through hydrogen bonding between specific blocks and other molecules in the blend. By properly tailoring the position of the blocks in the copolymer chain, it is possible to finely tune the repulsive or attractive interactions promoting the formation of non-classical morphologies.

Interestingly, selective engineering of the interactions with one block of the block copolymer template can work as guiding structure to control the spatial distribution of small particles or to control the absorption of specific molecules. The controlled placement of nanoparticles within block copolymers is of broad interest for the synthesis of functional nanostructured materials. Marsh et al. report about a new methodology to control block copolymer/nanoparticle interactions taking advantage of the so-called fluorophobic effect: fluorinated species strongly associate via repulsion from non-fluorinated media.<sup>[19]</sup> Placement of fluorinated nanoparticles within a block copolymer matrix with a fluorinated block was investigated as a function of the fluorophobic strength. This demonstrates the possibility to control nanoparticle position in the polymeric template, and paves the way to future controlled assembly of nanocomposites with multiple type of nanoparticles selectively segregated within specific block of the polymer matrix. Conversely, Malafronte et al. demonstrated that nanoporous polymeric templates obtained by block copolymer self-assembly can efficiently adsorb myoglobin.<sup>[20]</sup> The adsorption capability of the block copolymer-based support is mainly determined by the large surface area, the open pore structure and the trapping effect of the pores. The functionalization of surfaces with porous block copolymer thin films allow to tailor material properties for biomedical and biotechnological applications or to modify surface properties, achieving controlled level of hydrophilicity or hydrophobicity and determining surface area, roughness, and pore size distribution.

Looking at larger structure sizes, it must be remarked that capillary forces dominate all forces at sub-millimeter scale.<sup>[21]</sup> The combination of this favourable scaling with the ubiquitous availability of liquid interfaces in both natural and artificial settings has fostered the utilisation of surface tension-based effects in (self-)assembly, manipulation and actuation of a large variety of micro- and nanosystems.<sup>[22]</sup> Under specific

conditions capillary forces compete or even prevail over elastic forces, and the resulting elasto-capillary effects have been exploited to deploy a wide breadth of appealing structures including three-dimensional micro-electro-(opto)-mechanical systems and patterned polyhedral nanoparticles. In their paper Kwok et al. review the development of tailored elasto-capillary mechanisms for bending, curving and folding thin substrate films into various three-dimensional shapes.<sup>[23]</sup> These shapes can provide scaffold for or directly implement innovative functional systems with important applications in, e.g., bio-engineering, energy scavenging and micro/nanorobotics. The authors highlight that both theory and practice have reached such a level of development and sophistication that capillary self-folding stands as a uniquely suitable tool to address some otherwise prohibitively challenging tasks at sub-millimetric scale, and finally identify some interesting tracks for further advancements.

Moving to even larger scales, the contribution from Löthman et al. pertains to an intriguing class of works that aim to investigate whether macroscopic systems can be used to reproduce the phenomenology of microscopic or molecular systems or, conversely, the extent to which the thermodynamic description of the latter can be used to capture self-assembly in systems where gravity and inertia are to be reckoned with<sup>[24]</sup> – for the same reason that makes them observable without microscopes, i.e., size.<sup>[25]</sup> The authors present a study on a macroscopic fluidic system where spherical magnetic particles are suspended and interact thanks to a turbulent flow field. Having previously showed that their system can reproduce the Maxwell-Boltzmann statistics of particle motion in dilute gases,<sup>[26]</sup> here Löthman et al. analyse the functional analogy between temperature and turbulence as source of particle mobility respectively at molecular and macroscopic scale. They conclude that the crucial difference between the two lies in the isotropicity and power spectrum of the energy sources. The authors hypothesize that, though evidenced in a particular implementation only, similar caveat may apply to any sort of non-thermal shaking of a self-assembling system; and that, in spite of this, their system may find application as analogue macroscopic simulator for molecular dynamics and assembly.

In conclusion, top-down approaches admittedly provide precise control about structure at micro- and nanoscale. Conventional photolithographic approaches guarantee the possibility to create replicas of specific features with limited defectivity. This level of precision and reproducibility is remarkable, though it comes with important drawbacks, essentially related to its two-dimensional nature and the very-high cost, complexity and energy intensiveness of the production processes. In this respect, bottom-up approaches – particularly non-directed or non-templated – are intrinsically more defective than the most advanced top-down photolithographic processes used in nanoelectronics. Nevertheless, self-assembly stands as a general building heuristic, inherently much cheaper and more adaptable than lithography, which does not necessarily need supervision and provides the possibility to create complex three-dimensional structures within a rather simple technological environment.<sup>[27]</sup> It is worth reminding that nature usually builds extremely complex structures by self-assembly,<sup>[28]</sup> and biological systems in particular are constructed through

processes driven by encoding of information into macromolecules.<sup>[29]</sup> This simple observation suggests that this expanding and multi-disciplinary field of research could expectedly harbor the future possibility to achieve superior control and programming of matter at the nanoscale<sup>[30]</sup> and to develop novel paradigms in the way we build massive volumes of objects and devices. The works collected in this Special Issue represent a significant glimpse into the wide-ranging and far-reaching potential of bottom-up assembly. A long path of discovery and understanding is still necessary to master the full extent of that potentiality. Yet we believe that the collective effort of the different scientific communities tackling self-assembly from very different backgrounds will speed up exploration, systematization and dissemination of knowledge and promote the development of further, unique or unprecedented applications based on this fascinating concept.

Massimo Mastrangeli and Michele Perego

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