



The scale-up of material micro-structuring: a perspective

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The microstructure of materials is crucial for their behaviour. High-resolution microscopy, advanced spectroscopy and improved modelling have enabled researchers to analyse the microstructure's influence in detail. In addition, methods derived from semiconductor technology now allow researchers to prepare rationally structured materials. Microstructures were thus adapted from living organisms or *de novo* from physical insight in order to evoke specific behaviour in synthetic materials. Biomimetic materials exhibit the properties of their natural counterpart, for example, the adhesion of Gecko feet [1] or the photonic band gap of opals [2]. Designed materials can show previously unknown behaviour, e.g. a negative refractive index, as in artificial electromagnetic metamaterials [3].

To synthesize such “engineered materials”, structural information is derived from nature or modelling and then physically realized in the microstructure of the material. This requires a synthesis process very unlike traditional approaches from metallurgy or polymer technology; those enable the engineer only to bias microstructure. Information input is limited, and the resulting structure is a complex function of the process parameters. The free parameters only implicitly define average structural features. Individual elements (for example, the grains in a piece of steel) are stochastically distributed and have a random size distribution. This is insufficient for rational microstructure design, but often sufficient for the economical production of a material with a certain property.

In contrast, microfabrication technology provides full control of structure. The

technology was originally developed for the production of microelectronic circuitry, where each functional element is unique. Comprehensive information (in the form of a mask design) enters the fabrication process and is explicitly translated into structure. In the ideal case, the fabrication process is a conformal mapping of the design data on the target substrate. This is sufficient for rational microstructure design even with extreme complexity, but is usually an extreme waste for the synthesis of designed materials.

Typically, the structures in engineered materials are arranged in small unit cells that repeat to form a macroscopic material (Figure 1). Thus, replication is a first step towards the scale-up of designed materials. The expensive primary patterning is performed only once and on a limited area; large areas are structured by transferring this master to the substrate multiple times. Common transfer methods include photolithography, where light intensity is modulated by the master, and imprint or printing [4], where mechanical contact leads to deformation of the substrate by the master (Figure 2). Many functional structures are now routinely fabricated by replication, including mass products such as holograms. Replication is expected to become one of the key technologies in emerging fields like flexible electronics.

Replication limits fabrication to materials that can be photopatterned or imprinted. It does not solve the problem of three-dimensional structures, either: while two-dimensional replicas can be stacked

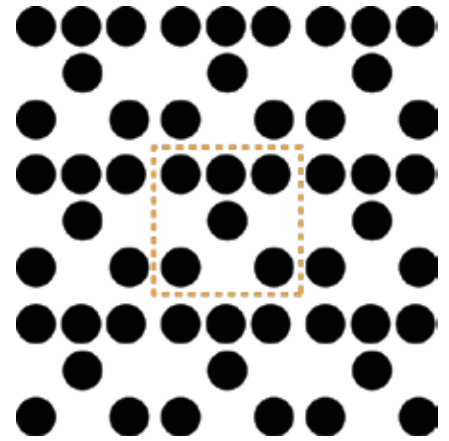


Figure 1: Many structured materials are composed of relatively small unit cells (marked in orange) that are repeated to form the bulk material.

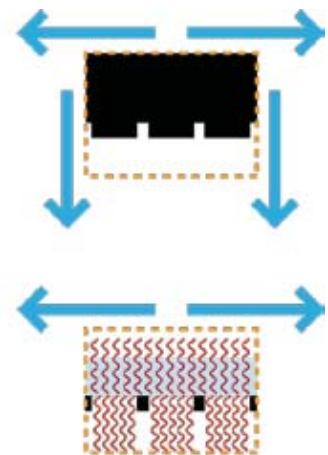


Figure 2: Replication methods, such as printing or imprinting (top) or photolithography (bottom) can be used to create large numbers or repeating unit cells.



on top of each other, this is far too slow to make macroscopic bodies and not suitable for any but the simplest three-dimensional structures. An alternative is to multiplex the patterning probe.

In a multiplexed approach, multiple parts of a material are addressed concurrently. The multiplexed probes can be the maxima of an interference pattern as in interference lithography (Figure 3) [5], or the synchronously moving tips of an Atomic Force Microscope (AFM) array (Figure 4) [6]. Interference patterns extend in three dimensions, thus enabling 3D fabrication. However, their geometry can only be modulated in a limited range. AFM arrays depend on many small tips that all have to work properly, are expensive and still rather slow. Such problems often plague multiplexed patterning. It is tempting to get rid of the probe altogether.

When parting with a central source of order, information has to enter the system on a different route. Because interaction lengths are limited, information has to be distributed throughout the ordering system. An elegant solution is to encode small building blocks so that they arrange through specific interactions. This is how viruses assemble in an infected cell: individual components are synthesized by the hijacked cell nuclei and assemble into the functional virus. In the inanimate world, supramolecular chemists synthesize molecules that interact to form complex superstructures. Similarly, colloidal particles have been found to interact with each other depending on their geometry

and chemical nature, thus forming complex nanostructures (Figure 5) [7].

It is intriguing that this principle works on many different length scales. A common problem in modern materials synthesis is hierarchical patterning. In many cases, macroscopic structures have to be combined with micron-scale and nano-scale features to obtain a certain effect. Biological systems master such multiscale synthesis easily because they synthesize materials from the smallest building units under molecular control. This is hard to mimic using conventional microfabrication. Components from different length scales that contain the structural information to form hierarchical structures are an interesting alternative. They can be optimized independently and combined in a modular fashion, an approach much more compatible to engineering principles.

Structure formation due to distributed information is often called “self-assembly” or “self-organization” [8]. As a synthetic tool, self-assembly is not as versatile as conventional microfabrication, and self-assembled structures often exhibit defects and lack long-range order.

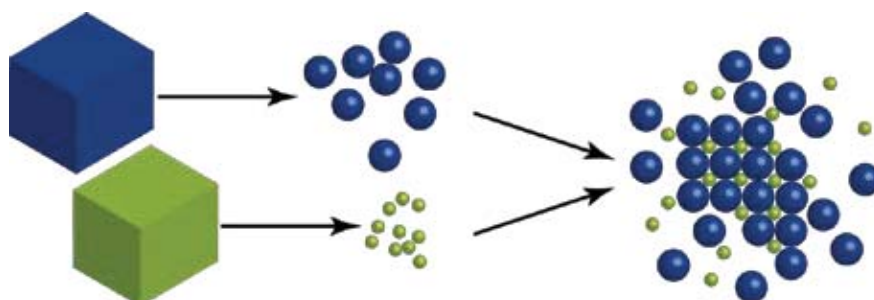


Figure 5: Certain mixtures of colloidal particles spontaneously arrange into ordered superstructures that depend on the particle geometries and interactions.

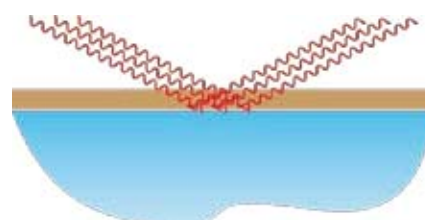


Figure 3: Interference lithography is based on overlapping beams of electromagnetic radiation that pattern a material due to the intensity modulations in the interference pattern.

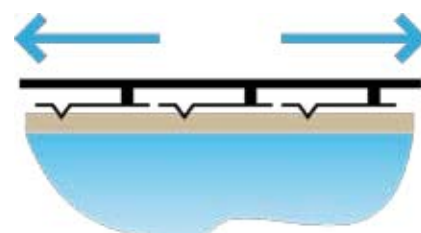


Figure 4: A multiprobe array (here composed of multiple AFM tips) writes identical structures at multiple positions in parallel.

It is, however, suitable for the synthesis of designed materials. Relevant for such materials are connectivity, symmetry, and termination, and self-assembly processes can efficiently generate those. For example, binary mixtures of nanoparticles form supercrystals with good short-range order and great structural diversity. The resulting materials exhibit interesting electronic properties notwithstanding the fact that the particle agglomeration process cannot produce long-range order [9].

Information enters the particle aggregation process mainly through the geometry and interaction potential of the involved particles. With increasingly narrow size distribution and structural uniformity of the involved particles and increasingly controlled processing, increasingly predictable structures are formed. The particle-based approach is convenient because particle geometry and interaction can be analysed and modified in great detail *a priori*, particles retain their identity and can be observed during the agglomeration process, and many different base materials can be shaped into particles. On the other hand, it is challenging because the quality of the constituent particles has to be very high, many interactions influence the aggregation process and the resulting structure have large interfaces that often govern their behaviour. The approach is not new: in food technology and cosmetics for example, particle aggregation has long been exploited to adjust texture.

It is as yet unclear which processes govern the assembly of nanoparticles into

ordered structures, or why certain structures form. In some cases, the reason will be simple energy minimization. The interacting particle system is ergodic and finds a minimum energy configuration in which it then settles. In many cases, however, this principle alone cannot explain the experimental results [7]. In addition, entropic effects are relevant. It is well known that the total entropy of certain, apparently ordered systems is greater than that of many disordered systems. Although the overall configurational entropy in the ordered arrangements is smaller, the entropy contribution of the individual particles can more than balance this reduction. Recent research tries to identify such arrangements using purely geometrical space-filling arguments [10]. If such arguments should hold, many different particle arrangements would be predictable and accessible simply by tuning particle size.

Not all particle ordering processes take place close to equilibrium or end in an equilibrium situation. On the contrary, the frequently used convective particle assembly process is a kinetically driven, non-equilibrium process. Hydrodynamic effects guide particles into their respective positions [11]. Fractal particle agglomeration is another classical mechanism of structure formation; only very short-range order can be generated by it, and the structures depend on particle transport rather than on particle structure. Such processes are very sensitive to process parameters like temperature and viscosity.



Process design is critical even for those structure formation processes in which an equilibrium state is reached. The motion of colloidal particles is slow compared to that of molecules, and its motion is affected by many more processes than that of molecules. Hydrodynamic instabilities, for example, can severely distort the particle order. In addition, structural information in ordering particle systems is less explicit than in conventional patterning processes, so that secondary minima or bifurcation frequently occur and give rise to unwanted structures. Thus, in contrast to classical microfabrication processes, self-assembly suffers less from inhomogeneities over large distances. Instead, typical defects involve drastic local and even global deviations from the desired structure. Suppressing such instabilities is the main challenge in nanoparticle assembly on large scales. It is indeed possible even in relatively simple and cost-effective setups [12], but it requires diligent process optimization and rigorous control of the conditions.

The development of scalable microstructuring technologies, from electron beam patterning to particle self-assembly, has the potential to make engineered materials available for mass applications. In that, it is similar to the development of chemical nanoparticle synthesis: a simple principle yields macroscopic amounts of nanostructures. Like in nanoparticle synthesis, the actual assembly process is rather complex and requires considerable know-how in scale-up. When it is understood, however, the process has the

potential for relevant technological innovation.

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