6. Templated Self-Assembly of Particles

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Nanoparticles are frequently immobilized on substrates to use them as functional elements. In the resulting layer, the particles are accessible, so that their useful properties can be exploited, but their positions are fixed, so that their behavior is stable and reproducible. Frequently, the particles' positions have to be well defined. Templated assembly can position particles even in the low-nanometer size regime, and it can do so efficiently for many particles in parallel. Thus, nanoparticles become building blocks, capable of forming complex superstructures.

Templated assembly is based on a simple idea: particles are brought to a surface that has binding sites which strongly interact with the particles. Ideally, the particles adsorb solely at the predefined binding sites, thus creating the desired arrangement. In reality, it is often a challenge to reach good yields, high precision, and good specificity, in particular for very small particles. Since the method is very general, particles of various materials such as oxides, metals, semiconductors, and polymers can be arranged for applications ranging from microelectronics to optics and biochemistry.

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Solid particles with sub-μm diameters are intriguing objects. They have a well-defined surface which is large compared with their volume, so that they interact strongly with their environment. At the same time, particles are clearly defined entities which can be mixed, purified, modified, and arranged into larger structures. This combination has made them popular in fields ranging from biology (where they carry analyte-binding molecules) to semiconductor fabrication (where they confine electrons) [6.1].

It is tempting to try and use such particles as nanoscale building blocks to create functional devices, be their function electronic, mechanical or chemical.

There are two prerequisites: first, particles with narrow size distribution and well-defined structures and surfaces have to be available from different materials in sufficient quantities. Second, these particles have to be arranged such that they provide the desired functionality. Templated particle assembly is one way to do so. A template defines the particle arrangement in advance according to the designer's wishes.

Producing particles of sufficient quality to be used as building blocks is not necessarily simple, but it can be done efficiently. Chemical methods are known to produce particles from very small clusters (with diameters in the low nanometer regime), various shapes of sin-

gle crystals with diameters from 10 to about 100 nm, and larger particles with diameters up to micrometers. Some syntheses produce particles that are rather monodisperse, the best methods reaching coefficients of variation below 3%. This is still worse than, say, the relative size distribution of bricks in most buildings, but good enough for the particle to arrange spontaneously into ordered supercrystals [6.2]. The particles can be simple crystals or complex structures with a shell that differs from the core, for example, to protect the surface of the core [6.3]. Chemical methods readily produce such core–shell structures which would be exceedingly complicated to make using conventional methods.

As for their arrangement, particles down to about 100 μm in diameter are routinely handled using conventional pick-and-place techniques, a method widely used in industrial processes. Such serial methods become very time consuming at smaller scales, and they fail in the sub-μm regime, where adhesion forces render the simple maneuver of *putting down* a particle very challenging [6.4]. In this size range, particles are dominated by Brownian motion. They move randomly in their suspensions, and alternative assembly methods become necessary for their placement. Templated particle assembly is such an alternative strategy, based on a predefined surface that carries the information on the final particle placement. It can produce a variety of particle arrangements in parallel and over large areas (with typical lateral dimensions up to 10^6 particle diameters).

Templated assembly utilizes the strong interactions of particles with interfaces and their tendency to produce dense packings to create predictable arrangements on a patterned surface. Since the desirable arrangement depends on the desired material properties, it is an advantage of templated assembly to give the user great flexibility in attainable particle arrangements.

There are rather different motivations for the use of well-defined particle arrangements. If single-particle properties are to be exploited (for example, their small size, large surface-to-volume ratio or optical properties), it is often critical to know in advance the exact particle positions. Particles are then commonly arranged into spaced arrays, possibly with alignment marks. In a biological assay, for example, a fluorescence reader can find the individual particles in a regular array according to their position and record their optical properties to gain information on an analyte that had come into contact with the particles [6.5]. Similarly, if par-

ticles are used as memory elements [6.6], they need to be electrically addressed – a task that is greatly simplified if their positions are well known in advance.

Interacting particles can exhibit collective properties that depend on their relative arrangement. In the field of metamaterials, for example, the activity of many particles with sizes well below the wavelength of an incident electromagnetic wave leads to unusual far-field behavior [6.7]. From afar, the bulk metamaterial appears to have, for example, a negative refractive index. Optical metamaterials also include photonic crystals, which exhibit a photonic bandgap much like the electronic bandgap of semiconductors due to a periodic potential caused by regular crystals of spherical, diffracting particles. Templated assembly can create such dense structures with well-defined boundaries, and it can influence the packing itself by imposing a desired geometry on the first layer.

More complex structures, possibly including more than one particle type, offer even more complex functionalities. One popular target is *smart materials*, which react to a stimulus in a coherent and useful way. Much like the electronic properties of a semiconductor microchip lead to extremely complex electronic behavior, patterned materials formed from arranged particles might exhibit useful mechanical, thermal or other properties. Another application of such complex structures (which are hard to produce) is anticounterfeiting, where an object is protected by a small particle structure with a unique property that can be detected.

Templated assembly is, of course, competing with more traditional means of micro- and nanofabrication, as covered in other chapters of this Handbook. Templated assembly is advantageous in that it takes advantage of the chemically produced small dimensions of nanoparticles, and it is more general than traditional methods in that it can process a wide variety of available colloids. The actual assembly process can be rather simple and compatible with continuous processing, even under ambient conditions. The most challenging prerequisite is usually the template, which has to be fabricated to provide sufficient definition of the assembled structure.

A process that arranges particles into a regular structure without any template is often called *self-assembly*. Here, the information on the arrangement is not contained in a template but in the properties of the particles themselves. The problem of *programming* the assembly process is thus shifted to the particles, which have to be chosen (or modified) such that they assemble into

a certain structure. This is not an easy task, and there are few examples so far of rational materials design using engineered particles. A template, on the other hand, can be defined using classical top-down methods, which provide great flexibility.

Still, templates become hard to fabricate if the particles are small and high patterning resolution is required. A combination of self-assembly and templated assembly is then useful: boundaries are defined by the template, but additional effects such as particle–particle, particle–surface or particle–solvent interactions lead to a predictable particle arrangement inside the boundaries.

We will limit ourselves here to processes with surface-bound templates and disregard supramolecular assembly, although molecular cages might also be regarded as templates. Likewise, biomineralization processes which can be templated using certain surfaces will not be covered here. The main focus is on sub-μm particles that are hard to place using any other method but can be assembled with high quality by means of templated assembly processes.

Even today, larger particles (between ≈ 1 and 100 μm) are assembled using templated assembly methods, mostly from slurries in an approach called *fluidic assembly* [6.8]. Illumina, Inc. arranges 3 μm-diameter glass beads functionalized with short DNA strands into a regular grid, which can then be used for DNA sequencing. Alien Technology Corporation holds several patents covering the integration of semiconductor pieces into polymers and other carriers, which today it mainly uses for the production of radiofrequency identification (RFID) chips, in which small electronic radiofrequency components are mounted on a paper or polymer label which is attached to an item for wireless identification. Similar methods for much smaller particles are currently being developed, but have not yet been applied industrially.

The challenges that occur when going down in particle size are mostly due to the greater influence of Brownian motion, which disturbs any order formed; strong adhesion to surfaces, which increases unspecific adsorption and makes pick-and-place difficult; and the problem of process control as the particles become harder to resolve with conventional optical methods.

In addition, the dimensions of the targeted nanostructured materials are often comparable to those produced with larger particles, but the number of particles involved is now very much higher (scaling inversely with the particle volume). Even assembly methods with very high yields are therefore bound to produce defects, which might hinder the function of the material. In some interesting applications (such as optical metamaterials), the absolute placement accuracies required to create a discernible optical effect are strict. Templated assembly is in principle able to provide such accuracies – even for many particles – and we will discuss its prerequisites in the next section.

6.1 The Assembly Process

Templated particle assembly involves particle adsorption on surfaces, and the well-developed ideas from adsorption theory (treated in many monographs and reviews) also hold for the case of templated assembly. While in many classical adsorption processes adsorption occurs at unpredictable positions, often until the entire surface is covered, the goal of a templated assembly process is the arrangement of particles with great precision and specificity. In this chapter, we will review some concepts that are less prominent in the adsorption literature. A useful metaphor of the directed assembly process is the energy landscape, which we will introduce here and frequently use to illustrate effects of interaction lengths, particle mobility, time scales, and other features of assembly methods.

6.1.1 Energy and Length Scales

A driving force that brings a colloidal object to a defined position and holds it there has to overcome Brownian motion. This constitutes the minimum requirement for the design of a templated assembly process. In the absence of a driving force, the particle will deviate from its original position r_0 according to

$$\frac{1}{3}\langle(r - r_0)^2\rangle = \frac{k_B T}{6\pi a \eta} t = 2Dt \,, \tag{6.1}$$

depending on the temperature T, the particle diameter a, the viscosity of the surrounding fluid η, the time t, and Boltzmann's constant k_B [6.9]. Thus, when averaging over a very large number of particles, a 10 nm-diameter particle in water would move about 51 μm in 60 s.

Table 6.1 Interactions that can drive particle assembly processes

Interaction	Typical range (order of magnitude)
Covalent	0.1 nm
van der Waals	1 nm
Coulomb (electrostatic)	1 nm (polar)–100 nm (apolar)
Hydrophobic	1 nm
Capillary	1 mm

The goal of an assembly process is to overcome this random, diffusional motion (with an energy scale of $k_B T$ and characterized by the diffusion coefficient D) by a bias that induces drift so that the probability of finding a particle at the desired position is markedly increased. Particles are then held in place until the system is quenched in some way, for example, by exchanging its environment.

In order to arrange the particles, templated assembly processes use potentials with minima at the particles' target positions. Such potential wells can be defined using various particle–surface interactions, some of which are listed in Table 6.1. These interactions act over different lengths, have different strengths, and form minima with different geometries, all of which can influence the assembly process.

Let us consider a particle that is moving in a fluid in the vicinity of a surface with *binding sites*, that is, features that interact with the particle more strongly than does the rest of the surface. The particle is mobile and moves randomly due to thermal excitation. Figure 6.1 illustrates this situation: depending on its position, the
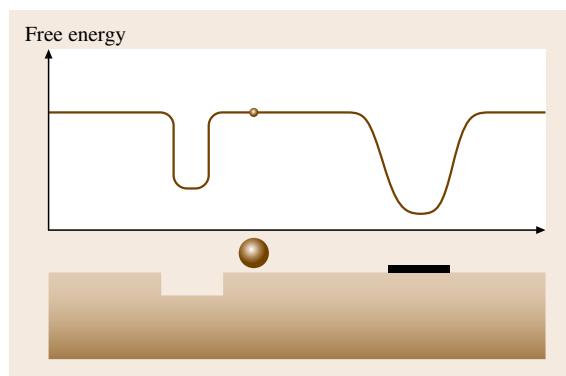
free energy of the particle will change as the interaction with the binding sites changes. If there is a gradient present, a directing force will act on the particle and bias its random motion towards an energy minimum. This *energy landscape*, formed by the superposition of the interaction, governs the particle's motion.

Some interactions are strong but short-ranged, for example, covalent bonds. In the energy landscape picture shown in Fig. 6.1, they will resemble a steep well into which the particle falls and from which it can hardly escape. On the other hand, the particle can be in close proximity to such steep wells and still not feel their presence. More precisely, the probability distribution of its presence will only be affected locally. When the particle is trapped inside the well, and if the entrapment can be reasonably modeled using a harmonic oscillator, its deviations from the minimum at $x = 0$ equals [6.10]

$$\left\langle x^2 \right\rangle = \frac{k_B T}{m \omega_0^2} \tag{6.2}$$

for a particle with mass m that is bound as in a harmonic oscillator with a frequency $\omega = \sqrt{k/m}$, the square root of the spring constant over the particle mass. Thus, a steep potential minimum can trap a particle with high accuracy: if the oscillator has a frequency of 1 GHz, a 10 nm particle of gold will deviate by less than a nanometer. The prototypical example of such a strong binding site is a topographical hole from which the particle cannot escape. The walls provide very steep exclusion potentials. Much less steep, but affecting a larger volume, is the well formed by an electrostatic field. In practice, even if the theoretical assembly accuracy of such an electrostatic binding site is limited, it often provides very good results. Other factors turn out to be critical as well – in particular the minimal achievable size of the binding sites and the yield of assembly. An assembled particle can simply block a binding site geometrically by not letting any other particle sufficiently close to the site, but it can also neutralize its charge (at least partially) and therefore hinder the adsorption of additional particles. Such changes in the energy landscape due to adsorption are often critical for the specificity and kinetics of the assembly.

Some of the most relevant interactions in directed assembly processes are summarized in Table 6.1. The exact shapes of the energy landscape caused by a particular interaction potential depend critically on the binding-site geometry, while the interaction lengths depend mainly on the used materials, solvents, and surfactants. Electrostatic interactions in suspensions are

Fig. 6.1 A particle moving in an energy landscape during templated assembly. Its trajectory depends on the shape of the potential wells created by the binding sites, which also influence yield and accuracy of assembly

subject to shielding by ions from the solvent; their strength can also depend on the hydrodynamic situation. van der Waals interactions depend on the dielectric properties of the solvent: their interaction length is generally so short that they do not *funnel* particles from the bulk but trap particles that randomly hit the surface or were attracted by other forces. Supramolecular interactions are not included here because they are too diverse; in general, such interactions tend to be similarly short-ranged as van der Waals interactions. In three-phase systems, capillary forces can occur and exert very long-ranged forces even on small particles.

An important practical limit of the assembly accuracy is the template. The template has to be fabricated, often using top-down methods, to define the final particle positions. It may have binding sites that are large enough for many particles to be trapped inside, either in ordered arrangements or in disordered layers. On the other hand, it may have binding sites that are small enough to accommodate only a single particle. If so, the area of a binding site usually has to be on the order of the particle's projected area. A particle that comes into contact with the binding site might be irreversibly adsorbed immediately. In the energy landscape picture, this would correspond to a well with steep walls and a flat base. On the other hand, if the well has slanted walls and a small base, the particle can align with the binding site with better placement accuracy (Fig. 6.2). If it is not possible to pattern the template with very small binding sites, one either has to accept limited placement accuracy or employ an additional *focusing* mechanism so that the particle will be deposited at a well-defined position inside the binding site. One example is the combination of electrostatic and capillary interactions [6.11].
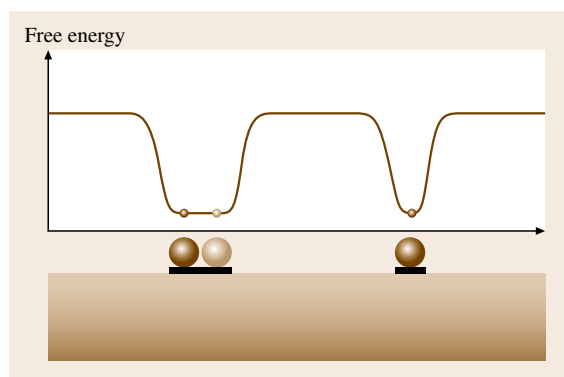

Fig. 6.2 Placement accuracy and yield depend on the geometry and potential shape of the binding sites

Various forces can occur in combination or subsequently during an assembly process. For example, in the classical example of the *convective assembly* of particles in a thin wetting film, hydrodynamic drag and capillary forces act in different stages of the assembly, yielding two-dimensional crystals of particles [6.12]. In templated assembly, one can use such combined effects to cause additional confinement. *Aizenberg* and her group have shown that the combination of capillary and electrostatic forces produces a *focusing* effect when particles are assembled on larger patches [6.11]. The energy landscape changes with time: its minimum becomes narrower as the liquid evaporates and centers the assembled particle on the binding site.

The formation of a potential *funnel* that guides the particle to its desired position is desirable for successful templated particle assembly. A properly chosen energy landscape ensures high placement accuracy, as discussed above. It also increases the yield of assembly by attracting particles from a larger volume towards the binding site. Assembly is more rapid if particles are guided from a larger volume instead of randomly diffusing until they accidentally arrive at the binding site. On the other hand, unspecific deposition is avoided if secondary minima on the energy landscape are kept shallow and are connected to the global minima (the binding sites) via low-energy pathways.

6.1.2 Mobility, Stability, and Yield

If the energy landscape is appropriate, a particle with sufficient mobility can explore it and assemble. With increasing mobility, it will (on average) find the binding site more rapidly and escape from secondary minima more easily, but it will also have a larger probability of escaping from the desired minimum. The probability for a particle with mass m to escape from the binding site that produces a potential well with local shape $\omega^2 x^2/2$ surrounded by valleys of height Q equals, in unit time [6.13],

$$P = \left(\frac{\omega}{2\pi}\right) e^{-mQ/(k_B T)} , \tag{6.3}$$

a result widely used in transition-state theory. This rate can be limiting for the assembly process, but it is more frequently the initial adsorption that requires most time. Colloidal particles and solvated molecules gain the mobility required to find binding sites through Brownian motion by collisions with the solvent molecules. Equation (6.1) describes the ideal situation of an infinitely dilute particle suspension, where no interaction between the particles exists. In practice, interactions are very

common at higher particle concentrations, and they influence the particle mobility according to [6.14]

$$D(c) = \frac{c}{1-c} \frac{(\partial \mu / \partial c)_{p,T}}{f(c)} , \qquad (6.4)$$

which gives the diffusion constant D as a function of the number concentration c, the chemical potential μ, and the friction coefficient f. If the particles interact strongly, the chemical potential will increase with increasing concentration, and so will the diffusion constant. At increased concentrations, the assembly behavior will then change. For gold colloids, the apparent diffusivity can be increased by two orders of magnitude at increased concentrations, but drop radically when the range of stable concentrations is exceeded.

Equation (6.4) is a thermodynamic expression, and the link to the microscopic events at a binding site in templated assembly is not trivial. A reduced diffusion constant can indicate a reduced escape rate from a binding site, but the thermodynamic value obviously does not hold when regarding a single particle, particularly if it is in the proximity of a binding site and encounters additional interactions. Statistical effects (as addressed in Sect. 6.1.4) are also not covered. Two consequences of particle interaction are particularly important: the potential required to increase the concentration of a colloid locally and the limited stability of colloidal suspensions.

Colloid scientists have long studied the case of interacting particles to derive expressions for colloidal stability. Smoluchowski and others derived expressions for the rate of agglomeration as a function of particle mobility and interaction, arriving at a characteristic time for doublet formation of

$$t_p = \frac{\pi \mu a^3 W}{\phi k_B T} , \qquad (6.5)$$

which depends on temperature T and viscosity μ [6.14]. The value is inversely proportional to the volume fraction ϕ of the particles and depends strongly on their diameter a and the interaction potentials (expressed via the stability ratio W). Doublets can thus form at time scales ranging from milliseconds to many hours, a very wide range that is reflected in the qualitative statement that a colloid is *stable* or *unstable* towards flocculation. A similar time scale will govern the templated assembly of particles. Different regimes occur, also depending on the hydrodynamic situation. The assembly can be purely Brownian (if there is no flow present), diffusion limited (for a rapid and efficient adsorption process at low concentrations and high surface densities) or reaction limited, if sufficient particles are present. The latter

is the most widespread regime in templated assembly that uses chemical patterns on a submerged template with sparse binding sites.

If multiple particles are to be assembled in a single step in close proximity, the same repulsive interactions that prevent agglomeration in the colloid have to be overcome to pack the particles densely. These forces are considerable. In a stable, aqueous colloid, the electrostatic repulsion, characterized by $e\psi_s$, will generally be greater than $10 k_B T$ and often around $100 k_B T$. Overcoming this barrier to reach the energy minimum caused by van der Waals interactions therefore requires a large driving force. Alternatively, the ionic strength can be increased locally to lower the electrostatic interaction and create a funnel through which the particles can reach the densely packed stage. If none of the above is present, sparse packing will result, described by modified random sequential adsorption models, as discussed later.

Many technological applications of self-assembled nanostructures, in particular those in electronics, require high yields of assembly and well-defined arrangements. This is in contrast to biological systems, where defects can be repaired through error-correction mechanisms. In the absence of such mechanisms, however, the yield of assembly has to be very high. This yield depends on the nature of the binding sites, the concentration of particles, and the characteristics of the assembly process. In particular, we can differentiate between *abrupt* assembly processes, where the actual particle deposition and its final immobilization (or quenching) occur almost simultaneously, and *gradual* assembly processes, where the two steps are not coupled. If the assembly takes place in the front of a receding meniscus that moves over a solid template, it will leave the particle dry and immobile, and if a binding site stays empty, there is no second chance for it to be filled. If the template is entirely submerged in the liquid, on the other hand, we can at least theoretically wait until every binding site is filled. For a rough estimate of the assembly rate, we can use Schurr's expression [6.15] for the particle flux J_s to a surface

$$J_s = c_s \sqrt{\frac{k_B T}{2\pi m}} , \qquad (6.6)$$

which assumes a Maxwell–Boltzmann-distribution to derive the flux from the particle number concentration at the surface c_s and their mass m. If we know the sticking probability S of the binding site, i. e., the probability for a particle to be adsorbed upon contact, we can directly calculate the half-life of an empty binding site.

If particles readily desorb from binding sites, an equilibrium situation will finally develop. The yield will then never reach unity, and its value will fluctuate over time.

6.1.3 Large Binding Sites

Consider a particle that hits a binding site with area A. If the particle gets sufficiently close to the site and if its interaction with the site is sufficiently large to overcome Brownian motion, the particle will be adsorbed. When we have a large number of such binding sites, particles will be randomly arranged inside the various A, so that the precision of arrangement is limited by the minimum size that (a) the template patterning can produce and (b) allows for sufficiently rapid particle assembly.

If, on the other hand, a funneling effect of the kind discussed above is present, the distribution of the particles might be biased towards a certain part of A. Then, the width of the position distribution is the result of the competition between a stochastic force (Brownian in general) and the directing force.

If the area A is large enough to accommodate multiple particles, particles can either arrange into random submonolayers or into ordered dense layers. The first case, particle adsorption on strongly adsorbing surfaces, is described reasonably well by the random sequential adsorption (RSA) model, which predicts a random particle distribution. Adsorption ceases when there is no space left in the binding area that could accommodate an additional particle. The final packing density is called the *jamming limit*, which can be numerically found to be $\theta_\infty \approx 0.547$ for two-dimensional, circular particles [6.16]. Random sequential adsorption is the subject of numerous reviews, which also discuss its application to anisotropic particle such as rods [6.17, 18].

The RSA model accurately describes many molecular adsorption problems, in particular the adsorption of proteins on surfaces. It does not cover processes that result in dense ordered arrangements, for example, self-assembled monolayers (SAM). In contrast to the RSA model, the molecules that constitute a SAM retain some mobility even after they are adsorbed on the surface. They interact with other molecules even before they adsorb, and they interact with the underlying metal film. Larger particles sometimes behave similarly. The rearrangement of particles in an evaporating liquid film due to capillary forces is a well-known example.

When dense ordered packings are desired, the particle–surface interaction has to be appropriate to avoid RSA-like adsorption. It turns out [6.19] that,

by tuning the strength of the interaction, particle arrangements between well-ordered layers and randomly distributed submonolayers can be obtained.

6.1.4 Thermodynamics, Kinetics, and Statistics

Diffusion constants scale inversely with the particle radius. The diffusion constants of nanoparticles are therefore much smaller than those of molecules. A 100 nm-diameter sphere moving in water will exhibit a diffusion constant D of approximately 10^{-12} m^2/s. Diffusion-limited processes with particles are thus slow, equilibrium situations can often not be reached in observable times, and the kinetics of the assembly process influences the assembly results. From an energy landscape point of view, it is not sufficient to provide a well-defined minimum in an appropriate position; the pathway to this minimum also has to be taken into account.

Most real template–particle systems will have complex energy landscapes with a variety of secondary minima and kinetic traps. A well-known example is a chemically functionalized surface onto parts of which particles should bind specifically. In practice, one finds unspecific deposition and a certain degree of particle accumulation, both caused typically by unspecific van der Waals-type attractions. Countermeasures include stirring, which increases particle mobility and keeps them from settling in secondary minima; rapid processing, which decreases the number of undesired particle collisions and thus the probability of reaching such a minimum; and washing, which removes weakly bound particles.

There is one limitation, however, that cannot be overcome by such mobility-increasing measures. When the number of particles in the volume affected by a binding site is small, the probability of finding at least one particle inside this volume will be small too. In the simple Poisson model of the situation, a volume V would contain a certain number n of particles with probability

$$W(n) = \mathrm{e}^{-\nu} \frac{\nu^n}{n!} \,, \tag{6.7}$$

where ν is the average number of particles in the volume, $\nu = Vc$ in the homogenous case. The probability of finding at least a single particle in this volume is therefore smaller than

$$W(n \geq 1) \leq \sum_{n=1}^{\infty} W(n) = 1 - \mathrm{e}^{-\nu} \,, \tag{6.8}$$

and the particle concentration has to be above

$$c_c \geq -\frac{\ln(1-\gamma)}{V} \qquad (6.9)$$

to guarantee a certain probability γ for a particle to be present. This limits the yield in assembly methods which only capture particles during a short period of time from the volume V: when there is no particle present, none can be assembled. When we regard a large number of binding sites and require a certain mini-

mum yield, say, 90%, the colloid concentration at the binding sites therefore has to be at least $c = 2.3/V$, independent of any further process details. This concentration can be provided either by an overall larger colloid concentration or (often more practical) by an additional, long-range force that acts on many particles, much like a funnel again. Electrostatic or hydrodynamic forces can increase the particle concentration locally, for example, at a three-phase boundary line, and enable sufficient assembly yields. We will see how this is done experimentally in the next section.

6.2 Classes of Directed Particle Assembly

There are many options and examples of how to assemble particles and small objects into templates. Depending on the synthesis and the material of the particles, and especially on the medium in which the particles are supplied, different strategies can be applied. Furthermore, the material of the target substrate can determine the assembly method to be used.

Nanoparticles can be synthesized and held in the gas phase by a carrier gas as an aerosol. At this point, they can be assembled directly from the gas phase onto a template (Fig. 6.3a). As a dry powder, nanoparticles tend to agglomerate into larger clusters due to strong van der Waals interactions, thus making it almost impossible to arrange patterns of individual particles. Therefore, submicron-sized particles are often delivered as suspensions in a liquid medium, especially when they were synthesized in liquid phase. Usually, nanoparticles are easier to stabilize in liquid, and particle agglomeration is prevented by surface chemicals creating a surface charge or by the addition of surfactants.

For assembly from the liquid phase we differentiate two cases: assembly from the bulk liquid onto the solid template (Fig. 6.3b) or assembly at the solid–liquid–gas boundary, i. e., at the meniscus of a liquid front moving

over the substrate (Fig. 6.3c). In the following subsection we will illustrate the different assembly strategies with some instructive examples.

6.2.1 Assembly from the Gas Phase

Particles can be assembled from the gas phase into a pattern by localized surface charges on a substrate, as in xerography. Here however, the fabricated patterns are considerably smaller than in a copier or a laser printer. The *latent image* of charges is produced in a thin-film electret by contacting a nanopatterned electrode with the target substrate [6.20, 21]. The electret material can be a polymer (poly(methylmethacrylate) PMMA or a fluorocarbon layer) or SiO_2. The flexible patterned electrode is made from a patterned silicone elastomer (polydimethylsiloxane PDMS) with a thin conductive gold layer evaporated on top [6.20] or from thin patterned silicon on top of a flat PDMS sheet [6.22]. The flexible electrode is brought into direct contact with the electret and the charge image is produced by an electrical pulse. Charge patterns can also be produced by sequentially writing with a conducting atomic force microscopy (AFM) tip [6.23], although in these exam-
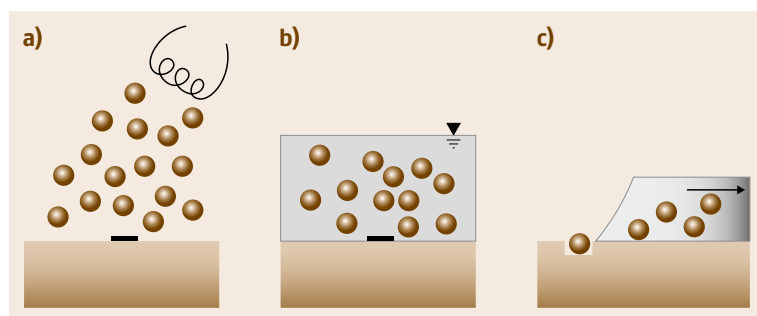

Fig. 6.3a–c Particles can be assembled from different media: they can be synthesized in a vacuum (or a gas) and directly assembled from the gas phase (**a**). Most commonly used are colloidal suspensions, from which particles are assembled at the liquid–solid interface (**b**). Alternatively, the particles can be assembled at the gas–liquid–solid boundary where strong capillary and confinement forces act on them (**c**)

ples the nanoparticles (NPs) were then adsorbed from the liquid phase (see the next section). The charge patterns are reported to be stable for more than 1 week in air [6.23]. Nanoparticle preparation is performed by an evaporative process in a tube furnace, by electrospray or in a plasma system [6.24]. Nanoparticles that have been synthesized in a wet chemical process can be used if they can be aerosolized without agglomerating. An interesting aspect is the combination of gas-phase particle synthesis with particle sorting methods, directly before the particles are assembled [6.25]. Almost monodisperse particle streams with few 10 nm-diameter nanoparticles can be prepared in this way. For the actual assembly, the nanoparticles have to be accelerated towards the target surface by an external field in a particle assembly module. Assembly of nanosized patterns from particles with a narrow size distribution can be achieved in this way.

Templates with an additional material contrast can improve the accuracy of particle assembly from the gas phase [6.24, 25]. The template is prepared from a patterned photoresist on a silicon substrate. In addition to the aerosol of charged nanoparticles, a stream of equally charged ions is introduced into the assembly chamber (Fig. 6.4). The ions are very mobile and fast compared with the nanoparticles and charge the resist structures on the substrate. The electric field of the charged resist pattern guides the nanoparticles into the areas of free silicon substrate. The additional ions improve the contrast between deposition in desired and undesired areas of the template (Fig. 6.5). By controlling the amount of ions it is possible to create and control a funneling effect which focuses the nanoparticles into structures much smaller than the actual template pattern. Among the smallest structures that have been realized by this method are 35 nm features assembled from 10 nm Ag nanoparticles in 200 nm holes (Fig. 6.6) [6.25]. In the majority of these assemblies, multiple nanoparticles are deposited into one assembly site and it is difficult if not impossible to assemble single nanoparticles with high yield.

6.2.2 Assembly in the Liquid Phase

In the majority of examples of templated assembly, particles are deposited from the liquid phase onto a solid template surface. Here, we want to differentiate assembly from the bulk liquid and assembly from the liquid at the liquid–solid–gas boundary (Sect. 6.2.3). For assembly directly from the liquid phase, a great variety of interactions such as electrostatic forces [6.26], capillary forces [6.27], for-
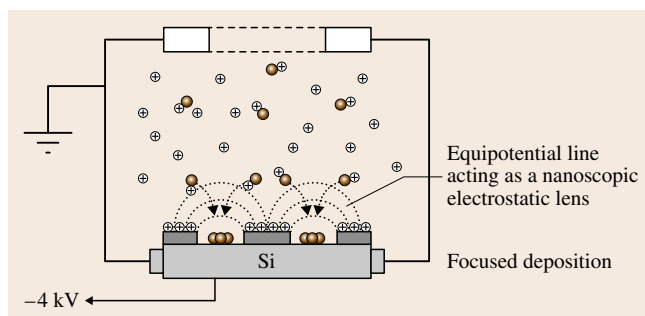

Fig. 6.4 Schematic setup for the assembly of nanoparticles from the gas phase in an electric field and with additional ions in the gas (after [6.25], © Macmillan 2006)
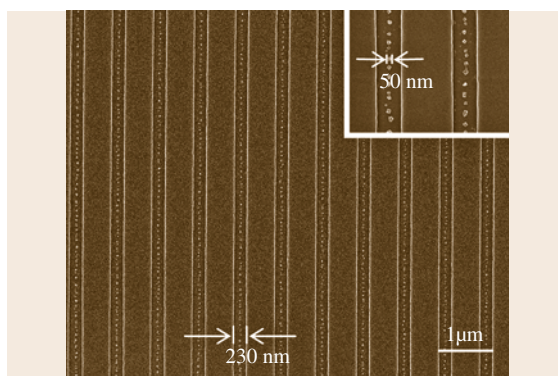

Fig. 6.5 Ag particles (10 nm) assembled in 230 nm-wide lines. The inset shows the funneling effect which reduces the actual width of the assembled particle lines to only 50 nm. The scale bar corresponds to 1 μm (after [6.25], © Macmillan 2006)
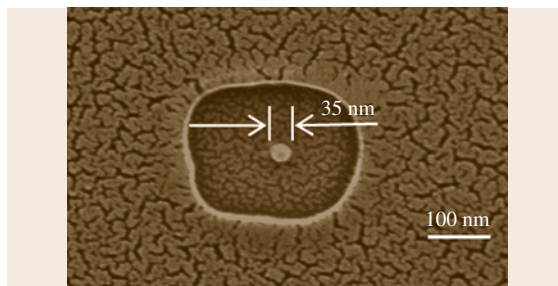

Fig. 6.6 Ag particles (10 nm) assembled in a 230 nm-wide hole. The funneling effect reduces the size of the actual assembly to only 35 nm. The scale bar corresponds to 100 nm (after [6.25], © Macmillan 2006)

mation of covalent bonds [6.28], specific recognition between biomolecules [6.29], supramolecular interac-
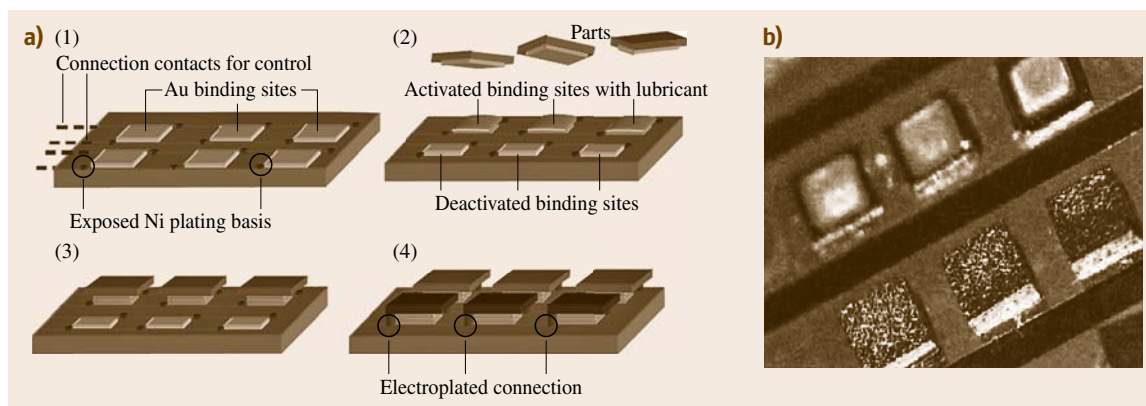
Fig. 6.7a,b Schematic description of the multibatch assembly process (1–4) with SAM-covered binding sites that can be deactivated selectively (**a**). A two-batch assembly result fabricated according to the scheme (**b**) (after [6.32], © IOP 2003)

tions [6.30], and form factor [6.8, 31] have been used. Also, electric fields can be applied to direct the particles or nanoobjects towards the targeted adsorption sites.

Wetting Contrast

For larger particles and objects, ranging from millimeters down to several tens of micrometers, wetting contrast in combination with capillary forces is applied for the assembly [6.27, 32, 33]. Topographic three-dimensional (3-D) features on the template may support the assembly in addition and introduce selectivity in a multicomponent assembly [6.34]. The template has hydrophobic assembly sites which can be selectively covered by a layer of adhesive or solder. The objects to be assembled are agitated in a fluid. In the simplest case – when a low-melting solder or a liquid organic adhesive is used – the fluid is water [6.35]. When higher temperatures are necessary to melt the solder, ethylene glycol [6.33, 34] can be used as a fluid. The suspended objects selectively adhere to the solder or adhesive when they come into contact. Objects to be assembled may also have a combination of hydrophilic and hydrophobic faces, which makes them adsorb with a preferred side or orientation. The strong capillary forces of the solder or adhesive guide the assembled objects into the desired orientation. The geometry of the adsorption sites and of the attached surfaces play a crucial role in this last step because local energy minima might freeze the assembled objects into undesired orientations on the template if the binding sites are not designed carefully.

Böhringer and coworkers devised a method in which hydrophobic assembly sites can be selectively

switched off and reactivated later for a second assembly step (Fig. 6.7) [6.32, 36]. In this way, different objects or particles can be assembled onto the same template sequentially. For this purpose, the assembly sites consist of gold electrodes which are covered by a hydrophobic alkanethiol SAM. The alkanethiol SAM can be electrochemically removed from individual electrodes in a selective manner. When dipped into an adhesive, only the hydrophobic SAM-covered sites of the template are wetted and covered with an adhesive layer. In the subsequent assembly step, only the adhesive-covered sites are active and can grab an object from solution. After the first particle assembly, all vacant electrodes can be modified with a SAM, simply by dipping into an alkanethiol solution, and the process can begin again.

Electrostatic Nanoparticle Adsorption

In liquid suspensions, particles are usually stabilized by surface charges. These surface charges prevent the particles from agglomerating and can be exploited to guide the particles by electrostatic interaction to adsorption sites of opposite charge. The template needs to display a contrast in surface charge. This can be achieved by microcontact printing of SAMs with charged end-groups [6.11, 37]. The pattern contrast can be further enhanced through layer-by-layer (LBL) adsorption of polyelectrolyte multilayers onto the printed monolayers [6.26, 38]. Microcontact printing of a polyelectrolyte pattern onto LBL multilayers also results in a pattern of different surface charge on the template [6.39]. Other methods based on nanoimprint lithography (NIL) and subsequent monolayer formation have been described as well (Sect. 6.3) [6.40].

On such charged SAM patterns, oppositely charged 10 μm-diameter gold discs adsorbed selectively onto sites of opposite charge [6.37]. The Au discs were modified by thiol monolayers to control their surface charge. Once the discs have adsorbed onto the surface of the template, there is no more mobility. The discs are fixed to their initial adsorption site. This lack of mobility prevents ordering in the layer of adsorbed discs. For the formation of an ordered monolayer a certain mobility of the discs on the template surface would be required. The same observation is made with smaller particles being adsorbed electrostatically. The adhesion forces are too strong to allow for any mobility of the particles on the surface. Thus, a well-ordered and densely packed layer of particles is inhibited. Well-defined arrays of particles can only be achieved when a single particle or a small number of particles per site are adsorbed. This was demonstrated for particles a few microns in diameter [6.26]. For smaller particles in the nanometer regime this is a very challenging task.

Polar solvents (water, alcohol) are usually necessary to stabilize the colloidal suspension of charged particles. However, additional ions in water have to be avoided since the surface charges of the template are more effectively screened with higher ionic strength in the solvent [6.37].

Sagiv and coworkers fabricated charged adsorption sites by means of writing with a conductive AFM into a self-assembled silane monolayer [6.41]. The otherwise inert monolayer is activated by the charged AFM tip, and functionalized molecules can be coupled onto the patterned areas (Fig. 6.8). The added molecules
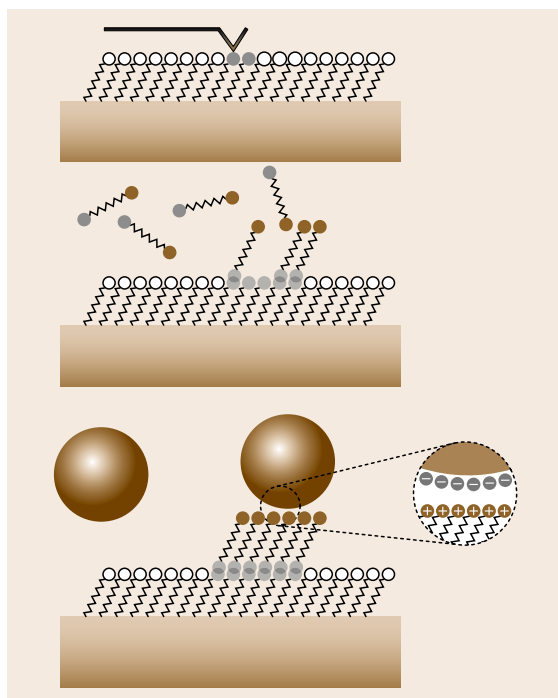

Fig. 6.8 Schematic representation of the modification of SAMs by AFM and subsequent bilayer formation to create assembly sites for selective adsorption of nanoparticles (after [6.41], © American Chemical Society)

can either carry a positive charge to attract negatively charged nanoparticles (Fig. 6.9) or carry a thiol group which binds to gold nanoparticles [6.28]. The latter
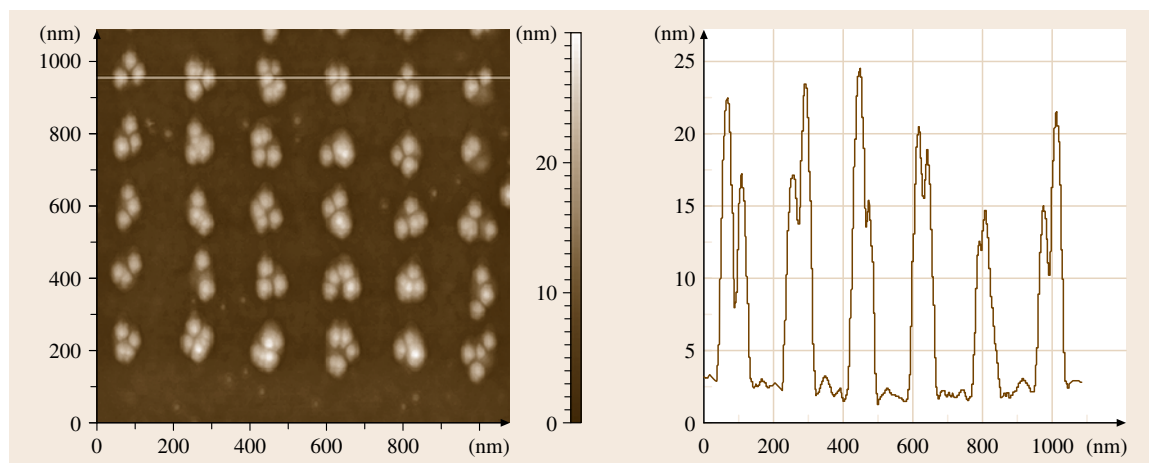

Fig. 6.9 Au particles (17 nm) assembled on amino-terminated bilayer templates (after [6.41], © American Chemical Society 2004)
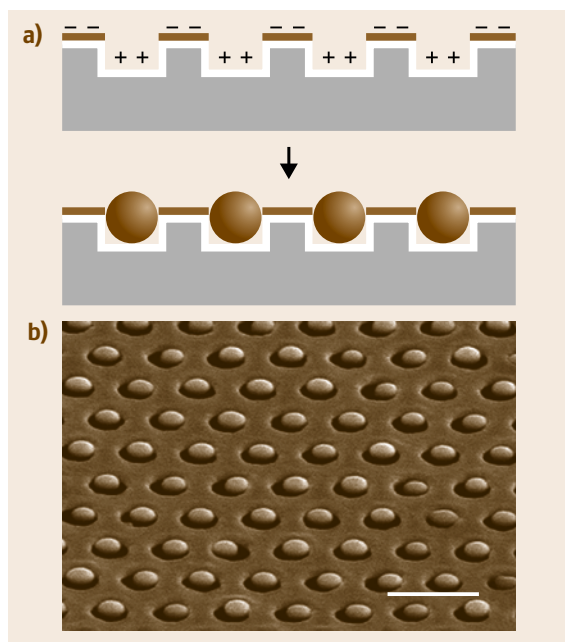
Fig. 6.10a,b Schematic illustration of the assembly of charged particles into a template of charge patterns with additional 3-D features (**a**). Scanning electron microscopy (SEM) image of 300 nm SiO$_2$ particles assembled into such a template with 450 nm-wide holes (**b**) (after [6.42], © Wiley-VCH 2007)

case constitutes an example of an adsorption mechanism where the particles are fixed to their adsorption site by a chemical bond and not by Coulomb interaction. In this case the directing force of the surface charge is not present. Due to the high lateral resolution of the AFM it is possible to create very small patterns of just a few tens of nanometers. Still, the adsorption of several nanoparticles per site is routinely observed on these templates.

Aizenberg and coworkers [6.11] published an assembly method that makes use of a combination of electrostatic adsorption and capillary forces. First, the particles are attracted towards charged monolayer sites. Then they are *focused* onto the sites by capillary forces when the solvent dries. In this work, the charged monolayer sites were also prepared by microcontact printing of charged thiol molecules.

Charges deposited into a surface of an electret can also act as a template for the assembly of nanoparticles. As in nanoxerography (see the previous section), the electret can be a polymer or a surface oxide layer and the charge pattern can be formed by a conformal electrode [6.20]. To create very small features in the nanometer range, charge is written by a conductive AFM tip [6.23]. Oppositely charged nanoparticles adsorb and adhere to these features. In the case of charges deposited into an electret, only nonpolar solvents such as fluorocarbons can be used. In water, the charge patterns would be neutralized rapidly [6.23].

A typical example [6.42] combines electrostatic patterns with 3-D geometry to define the location and number of adsorbed particles with higher precision. A nanostructured polymer template with 450 nm-wide holes was covered with alternating polyelectrolyte layers by LBL. In the final step, a negatively charged polyelectrolyte layer is printed onto the (positively charged) template with a flat stamp (Fig. 6.10). Thus, only the elevated parts of the template become negatively charged, while the depressions still carry a positively charged polyelectrolyte layer. Nanoparticles with negative surface charge are attracted towards the holes of the template. However, now the number of particles per adsorption site and their exact location is determined by the 3-D geometry of the adsorption site (Fig. 6.10).

Specific Interactions

It is sometimes desirable to have particles and binding sites interact more specifically. Certain surface modifications on the binding sites will only interact with appropriately coated particles. Of course, such *specific interactions* are ultimately based on the standard set of interactions such as Coulombic and van der Waals interactions or hydrogen bonds. However, by steric conformation of the interacting entities, selectivity towards a small set of binding partners or even towards a single species arises. As examples, we discuss supramolecular interactions of small hydrophobic groups with cyclodextrins [6.30, 43] and DNA hybridization [6.29]. Both types of interactions are short-range compared with electrostatic forces. Thus, the particles have to come into close vicinity to the binding sites either by diffusion or by other transport mechanisms, e.g., through agitation. While the interaction of molecular subunits with the cyclodextrins is selective and depends on the size and polarity of the guest unit, DNA hybridization is selective towards the exact composition, and only the exact counterpart to the offered sequence is recognized and adsorbed onto the binding site on the template.

In the case of cyclodextrin as recognition species, a monolayer of the cyclodextrin units is patterned onto a surface. This can be done by nanoimprint lithography, which can expose just a fraction of the substrate surface for the formation of the cyclodextrin mono-

layer [6.30, 43]. Nanoparticles with guest functionality such as ferrocenyl-functionalized silica particles bind selectively to the cyclodextrin-functionalized areas of the substrate [6.43]. Even 3-D structures can be built up sequentially using alternating layers of host- and guest-functionalized particles [6.43].

For DNA recognition, a pattern of single-stranded DNA has to be prepared on the substrate. This can be done by photolithography [6.45] or, for smaller feature sizes, by dip–pen nanolithography (DPN) [6.46]. Gold nanoparticles functionalized with a thiolated DNA strand complementary to the DNA on the template adsorb from solution specifically to the patterned binding sites through DNA hybridization. Usually, the surrounding substrate area has to be functionalized with a second monolayer that prevents nonspecific adsorption of DNA-modified nanoparticles [6.45].

An interesting variant of DNA-mediated assembly is the assembly of nanoparticles onto specific locations of DNA tiles [6.29]. DNA tiles are DNA objects that are formed by assembling smaller subunits into large sheets [6.47] or by folding a long single-stranded DNA with the aid of shorter pieces of DNA (*DNA origami*) [6.48]. DNA tiles can be designed with single-stranded DNA pieces at specific locations. Such a DNA tile with a pattern of single strands can act as a template for the adsorption of nanoparticles functionalized with the complementary strand [6.29, 49]. DNA tiles can also carry a pattern of other specific binding sites such as biotin functionalities. In this case templated assembly of streptavidin-functionalized nanoparticles can be carried out [6.50]. The adsorption of nanoparticles onto specific sites of DNA tiles allows for very high resolution in the assembly. However, the problem of assembling the DNA tiles and DNA origami structures themselves onto solid supports at specific locations with designated orientations is not yet fully solved. An interesting approach to this problem using dielectrophoretic assembly is described by *Kuzyk* et al. [6.51].

Dielectrophoretic Assembly

In dielectrophoresis, particles in a solvent are attracted to or repelled from a nonuniform alternating-current (AC) electrical field. The strength and direction of the dielectrophoretic force depends on the dielectric properties of the particles, solvent, electrode configuration, voltage, and frequency. By appropriate design of the electrodes, particles can be forced to desired areas on the template. However, if there is no additional persisting force, the particles leave their positions as soon as the AC field is turned off. *Suzuki* et al. applied a combi-
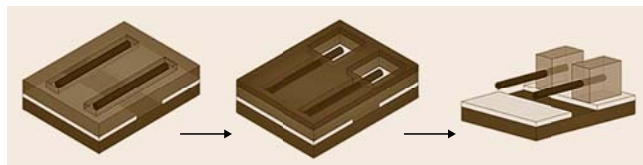

Fig. 6.11 Schematic illustration of the dielectrophoretic assembly of nanowires onto a template with additional 3-D structures formed in a resist. After assembly, the correctly assembled nanowires are fixed in a plating process and the resist is removed (after [6.44], © Macmillan 2008)

nation of dielectrophoretic assembly and covalent bond formation to overcome this problem [6.52]. The system was designed in such a way that $3\,\mu m$ polystyrene particles were guided towards areas of weakest electrical field, which was directly underneath the lines of an interdigitated electrode array on the opposite substrate. There, the particles were permanently bonded by a chemical reaction.

Dielectrophoretic assembly lends itself very well to the assembly of nonisotropically shaped objects such as nanorods or nanowires. The electric field can additionally align the wires in a desired orientation. *Mayer* and coworkers have applied this method to align semiconductor and metal nanowires on substrates [6.44]. The electrodes were covered with photoresist, which had openings at the desired binding sites (Fig. 6.11). Nanowires were directed to and adsorbed onto those sites. The topographic structure of the assembly sites helped to maintain the wires in the correct positions upon drying. The assembled wires were fixed in a plating process and lift-off of the resist layer removed those nanowires that adsorbed onto undesired positions. This combination of methods can significantly reduce the error count and increase the yield of the assembly process (Fig. 6.12).
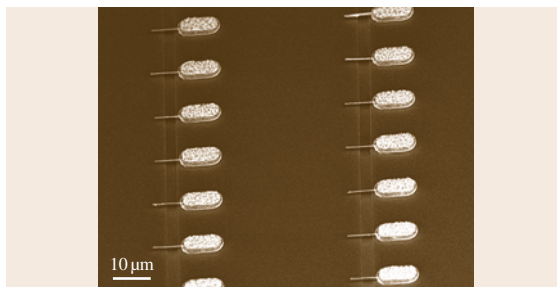

Fig. 6.12 SEM image of rhodium nanowires assembled using the process depicted in Fig. 6.11. The scale bar is $10\,\mu m$ (after [6.44], © Macmillan 2008)

A very versatile variant of dielectrophoretic assembly was demonstrated by *Chiou* and coworkers [6.53]. They fabricated an assembly setup with rewritable electrode patterns on a photoconductive surface. Simply by projecting an image through a microscope lens, they could define their electrode pattern for dielectrophoretic assembly of 4.5 μm latex beads.

When NPs are assembled from aqueous suspensions, drying is always a critical step where strong capillary forces of the drying droplet may act on the assembled particles and destroy or alter the assembled pattern. On the other hand, the strength and directing capacity of capillary forces may be exploited to control the assembly of nanoparticles very accurately, as shown in the next section.

6.2.3 Assembly at Gas–Liquid Interfaces

At the phase boundary between a colloidal suspension, the template, and the surrounding air, very strong capillary forces may act, depending on the solvent composition used. In many microelectromechanical systems (MEMS) those capillary forces are detrimental to the fabricated microstructures and drying is a very critical step in MEMS fabrication. However, those strong directing forces can be exploited very well for the assembly of particles onto a template.

When the meniscus of an aqueous particle suspension gets pinned on a surface it deposits the particles at the phase boundary in monolayers and multilayers onto the substrate. Convective flow of water transports even more particles towards the edge of the drop, thus forming the well-known coffee-stain-like patterns [6.57]. When the convective flow of water towards the meniscus can be controlled, it is possible to assemble particle monolayers or multilayers in a reproducible manner [6.56, 58]. Particles can even be assembled in spaced arrays when the meniscus only gets pinned at some specific locations on an otherwise smooth and nonwetting substrate. Such pinning locations can be formed by geometric features on the substrate, by a pattern of wetting spots, or by spots of increased particle–substrate interaction. Many researchers have exploited this mechanism for templated particle assembly with different setups (Fig. 6.13).

In most examples of this kind of assembly, the particles are dispersed in an aqueous colloidal suspension. Often, these suspensions contain surfactants to further stabilize the colloids and prevent them from agglomeration and precipitation. When the meniscus of such a particle suspension sweeps over a flat nonwetting surface, no particles are left on the substrate. The meniscus acts like a doctor blade, moving the particles over the surface. At geometrical features on the substrate such as a hole or the step of a raised structure, the water meniscus gets pinned and capillary forces can drive particles into holes or corners.

In the simplest experimental setup, a drop of colloidal suspension is left drying on a topographically
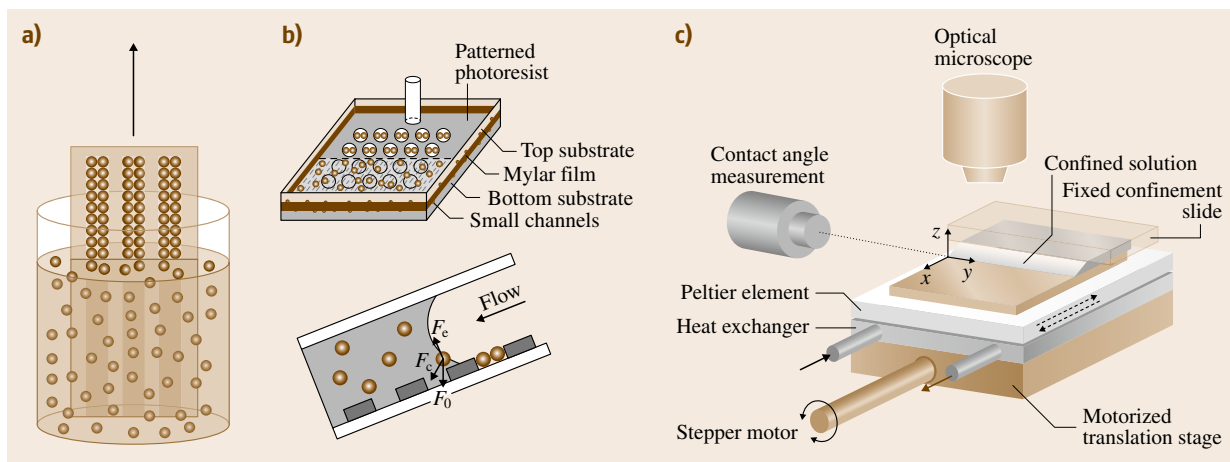
Fig. 6.13a–c Schematic depictions of capillary assembly setups: **(a)** dipping the template into the particle suspension and slowly pulling it out (after [6.54], © Wiley-VCH 2005); **(b)** assembly in a fluidic cell with a constant flow of particle suspension (after [6.55], © American Chemical Society 2001); **(c)** assembly on a motorized stage with controllable assembly speed and temperature (after [6.56], © American Chemical Society 2007)
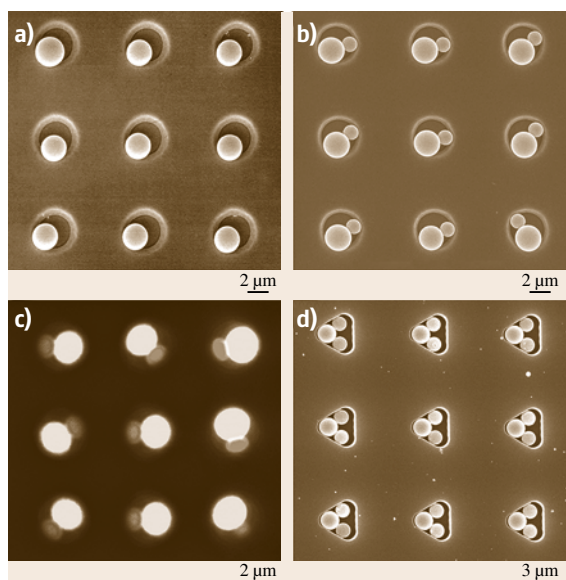
Fig. 6.14a–d Images of particles of different sizes assembled into holes with the device illustrated in Fig. 6.13b (after [6.55], © American Chemical Society 2001)

patterned template. As water evaporates the meniscus of the drop sweeps over the template and deposits particles into geometric features on the template. Here, there is only minimal control of the yield and evolution of the deposition process. At the start of the process, a low concentration of particles will be present at the meniscus. Then, with increasing evaporation, more particles are driven to the edge of the drop with the flux of water, and the assembly yield will increase. Finally, as the particle concentration in the drying drop reaches higher values, particles start to agglomerate and deposit in large aggregates. Thus, this simple method only supplies a relative small fraction of the template area with the desired assembly result.

Better assembly yield is achieved by placing the template (almost) vertically into a container of the colloidal suspension (Fig. 6.13a) [6.60]. As the solvent slowly evaporates, the meniscus moves over the template and deposits the particles in a controlled manner. Particles as small as 2 nm in diameter have been successfully assembled into template features of several 10 nm by this method [6.60]. Still, there is no direct control of particle concentration during the assembly and little possibility to react to changing parameters. Better control can be gained by pulling the template in a controlled manner out of the flask of colloidal suspension [6.54, 61].

Xia and coworkers designed a fluidic cell where the colloidal solution is sandwiched between the template and a cover slide (Fig. 6.13b) [6.55, 62]. A thin frame of Mylar film defines the distance between template and cover slide and controls the flow rate at which the dispersion flows through the cell. Depending on the ratio of particle diameter and template geometry, very regular and reproducible arrangements of particles in the assembly sites ranging from pairs to tetrahedral packings can be achieved [6.55]. When the assembly procedure is repeated with a second batch of smaller particles, assemblies of pairs of different particles in the same adsorption site are possible (Fig. 6.14) [6.55].

With a tool that controls colloid temperature and speed of meniscus movement, and allows direct observation of the assembly process through an optical
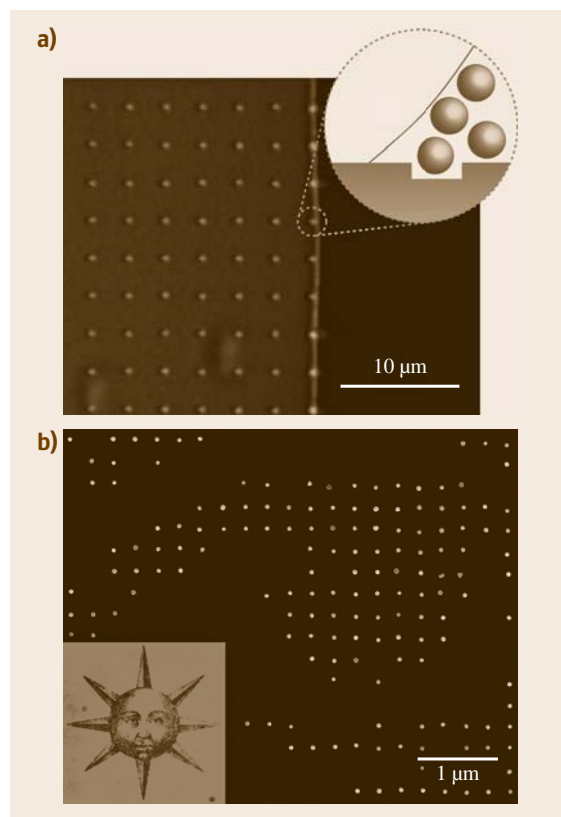

Fig. 6.15a,b Optical micrograph of the assembly of 60 nm Au particles into 3 μm-spaced holes. The bright accumulation zone is clearly visible. **(a)** Optical micrograph (inset) and SEM image of 60 nm Au particles assembled in a setup as illustrated in Fig. 6.13c and transferred to a silicon wafer (after [6.59], © Macmillan 2007)
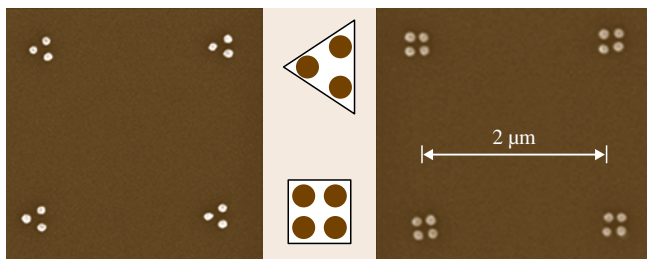
Fig. 6.16 SEM images of isolated 100 nm Au particles after removal of the template. The arrangement of the nanoparticles is determined by the geometry of the template (schematically depicted *in the middle*) (after [6.63], © American Institute of Physics 2006)

microscope, immediate response to changing conditions during assembly is possible (Fig. 6.13c) [6.56]. The template is mounted horizontally on a computer-controlled movable stage with a heatable vacuum chuck, and the colloidal suspension is sandwiched between the template and a glass slide. Observation of the assembly process from above reveals that for good yields a high concentration of particles is required at the meniscus. Particles are transported towards the meniscus by the flux of water in the same direction. As the temperature is increased, the evaporation at the meniscus increases. This causes an even greater flux of water and particles towards the meniscus. Lowering the temperature reduces the water flux and allows the particles to diffuse away from this so-called accumulation zone into the bulk solution. Consequently, assembly yield

drops dramatically. Upon renewed increase of temperature and particle flux, the accumulation zone is reestablished and assembly reaches high yields again (Fig. 6.15).

The templates used in this kind of assembly method mostly have topographical (3-D) features that capture the particles. Also, templates which only rely on a chemical contrast have been described [6.54, 61]. The particle trapping relies on electrostatic interactions in this case and many of the adsorption sites also capture particles from the bulk solution [6.19], as described in the previous section. Thus, in the case of templates with chemical patterns, there is a combination of trapping mechanisms. Often, areas prepared for particle adsorption carry a hydrophilic surface functionality which causes lower contact angles in these areas and particle trapping in a mechanism closer to convective assembly.

Combinations of geometrical trapping and wetting contrast are possible too. With a well-designed balance of geometrical features and wetting contrast, it is even possible to control nanoparticle placement within the adsorption site [6.63]. When the adsorption site is large enough, particles are dragged into its corners and thus well-separated particle assemblies in a triangular or quadratic arrangement can be achieved (Fig. 6.16). This can be regarded as a kind of hierarchical assembly, where the assembly mechanism helps to form a substructure with features smaller than those of the actual template.

6.3 Templates

The template carries the positional information on particle arrangement. In most templates used today, there is a simple relation between the position of a binding site and the final particle position. The binding site might be larger than the particle's footprint or differ from its shape; it might accommodate just a single particle or a large number of particles. When working with very small particles, its shape might be irregular due to the limited resolution of the patterning process. The assembly process translates this geometry into a particle arrangement, as discussed in Sect. 6.1. Still, the relation between template and particle position is simple: there has to be a feature on the template exactly where a particle is intended to be placed. Thus, the patterning technique used to make the template has to define the particle locations with an accuracy that is within the range of the particle's dimensions.

Some assembly processes are more complex. A particle might only be deposited on one side of a binding site, only in its center (even if there is enough space for multiple particles around it) or multiple particles might fill a larger binding site with a regular structure. This can be desirable: the fabrication of the template is usually easier if the critical dimensions do not have to be identical to the particle's diameter. In the ideal case, the template pattern would be easy to fabricate but define the desired assembly of very small particles unambiguously, whereupon the assembly process would translate it into a very high-resolution energy landscape for the particles to occupy. If the desired arrangement is very complex, the template will generally have to be rather complex too, but most practical arrangements are highly repetitive and modular, and could be encoded efficiently.

Many assembly templates are fabricated by means of top-down micro- and nanofabrication. The patterns are usually designed in a computer, transferred to a mask (often via electron-beam or laser direct writing), and converted to chemical or topographical patterns on the template surface. The typical resolution limit for templates formed using typical ultraviolet (UV) lithography is around 1 µm, although smaller structures are achievable if artifacts are acceptable. Smaller structures can be written using electron-beam (e-beam) lithography. While photomasks for UV photolithography (produced in large e-beam writers) are readily available commercially, sub-µm e-beam patterns in other materials are less common, and the sequential nature of e-beam writing makes the patterning of large areas time consuming and costly. Electron-beam patterning is very flexible, however, and is widely used for research purposes.

If the primary patterning method is costly, replication techniques are useful both to produce multiple templates from one primary pattern and to cover larger areas with a repeated pattern. For patterns below the optical diffraction limit, molding and printing are popular methods. The primary structure is used either to imprint a polymer layer at increased temperature and under pressure (nanoimprint lithography) or to shape a liquid prepolymer while it is curing (molding, UV imprint lithography, and others). Although some top-down methods directly produce chemical patterns, for example, by oxidizing UV-sensitive monolayers in photolithography or with an e-beam, the most common product is a topographical pattern. Soft lithography is a route both to replicate such a pattern and to convert it to chemical contrast: a silicone prepolymer mixture is cured on the topographical pattern, cured to a solid rubber, and used as a stamp with the inverse pattern. This stamp can then print molecules on various surfaces, a process named microcontact printing.

Even e-beam writing is limited to minimum feature sizes in the range of tens of nanometers. Smaller structures can be formed using probe methods. For example, the tip of an atomic force microscope can mechanically remove (scratch) a monolayer or oxidize its functional groups locally. The resulting template cannot be replicated easily, which makes the process rather uneconomical, but it provides extremely high resolution, for example, for the arrangement of metal clusters in lines to investigate their conductivity.

An efficient alternative to e-beam writing for the patterning of larger areas is the use of interference lithography techniques. They only produce regular interference patterns, but they can do so over large areas in a single exposure step. If small structures are to be created, the radiation wavelength has to be low, its intensity high, and its coherence sufficient. An excellent source is synchrotron radiation. Larger patterns are straightforward to create using simple laser interference. Other efficient routes to certain template geometries include wrinkling patterns and step edges that form when crystals are cleaved along high-index planes. All these templates are limited to specific geometries and, thus, create specific particle arrangements.

6.3.1 Chemical Templates

Chemical templates display a pattern of selective surface chemistries with areas that prevent particle adsorption and others that support it. Additional geometrical features are not necessary per se but can be helpful to increase selectivity. A simple wetting contrast (e.g., hydrophilic patches on a hydrophobic substrates) can be sufficient to assemble colloidal particles at the three-phase boundary [6.61]. In this case, the hydrophilic spots have to be large enough ($> 25\,\mu m$) to cause a significant lowering of the receding contact angle and deposition of particles. Chemical patterns with features of several micrometers can be fabricated by optical lithography. After exposure and development of the photoresist on a Si/SiO_2 surface, the exposed substrate areas can be treated with a silane molecule. Upon removal of the remaining photoresist, a chemical pattern (bare Si/SiO_2 surface versus silane surface) is achieved. For higher-resolution features, nanoimprint lithography or e-beam lithography can be utilized to pattern a polymer resist layer. Again, the accessible substrate areas can then be patterned by a specific surface chemistry, and subsequent removal of the polymer resist provides the template. The areas of bare substrate may also be covered by a surface chemistry orthogonal to the first one (hydrophobic–hydrophilic, anionic–cationic) in order to increase assembly contrast [6.40]. Alternatively, the polymer resist might not be removed at all, thus providing an additional 3-D feature to support assembly onto the template [6.40].

Microcontact printing of organic monolayers is also a viable method for the fabrication of surface-chemical patterns on oxide or noble-metal surfaces. Depending on the quality of the stamp material and architecture, even sub-µm patterns are attainable [6.64].

Many examples of chemical templates do not only rely on a wetting contrast, but provide real adsorption sites for the particles. This can be achieved by pattern-

ing a charged molecule or a polyelectrolyte layer, which then attracts the particles by electrostatic forces or with specific supramolecular interactions [6.43, 54].

Self-assembled structures of block copolymers on surfaces can also act as a chemical template when nanoparticles selectively adsorb onto one block of the polymer [6.65].

6.3.2 Charges and Electrodes

Electric charge can be brought onto a surface by means of an electrode. This is the principle of xerography, which has been scaled down using electrically conductive AFM tips to write very small charged areas onto the surface of a dielectric. The charged regions attract particles, which then assemble on the written patterns [6.23]. Small tips (readily available in an AFM) enable high resolution to be attained, although the actual charge pattern can deviate from the intended design.

Actively driven electrodes are the most versatile option for electric-field templates. They require considerable effort in terms of interconnections and electrode design and one has to avoid particle attractions to the wiring, but they can be actively switched. What is more, AC potentials can be applied, so that dielectrophoresis takes place. Nanoparticles [6.66] and nanowires can thus be aligned with two electrodes and can then be connected [6.67]. The electric leads for both assembly electrodes and device interconnects (which can be identical) are fabricated using standard microfabrication techniques. If necessary, they can be combined with additional topographical features, for example, to improve alignment in the assembly of anisotropic particles [6.44].

Dielectrophoresis can also be driven by an external electromagnetic field that is projected onto an appropriate substrate [6.53]. The projected image, microscopically demagnified, causes the assembly forces. Such an image can be modulated and is far more flexible than patterned electrodes; it can even be time dependent to further optimize the assembly process. Its resolution is, however, diffraction limited.

6.3.3 Topographical Templates

Purely topographical templates guide particle assembly by geometrical exclusion and by modulating other forces, for example, capillary interactions. Geometrical confinement can be very precise – the particle cannot enter a template wall – but it is limited by template precision. Compared with electrodes or chemical patterns, topographical templates are simple in structure and fabrication and can be replicated via molding and imprinting techniques.

Topographical templates are used in convective [6.56] and capillary particle assembly [6.62], as an additional guide to the crystal structure in electrophoretic particle assembly [6.68], and as an additional guide in dielectrophoretic assembly [6.44]. In all these cases, the geometries are very simple: holes of uniform depth in an otherwise continuous layer. In most cases, the structures are formed in photoresist by standard UV lithography and used without further processing. If the resist sits on top of a wafer, it is simple to create an additional wetting contrast between the (polymer) top surface and the (silicon oxide) bottom surface of the template holes.

More complex geometries are required to precisely tune the forces in capillary assembly. Step edges, crosses, corner shapes, and other well-defined obstacles trap particles in reproducible arrangements. Such templates are harder to fabricate than holes. They can, however, be replicated in polymers, such as polydimethylsiloxane (PDMS). A single silicon master can then produce many (up to several hundred) single-use assembly templates.

Polymer molding is also the basis of the microfluidic ducts used as templates in the micromolding in capillaries (MIMIC) process. These channels, in which particles are arranged from a microfluidic flow, are first formed as lines in ultrathick resist and then replicated in PDMS. The soft silicone replica adheres to flat surfaces, forming channels into which the particle suspension is sucked by capillary forces.

6.3.4 Advanced Templates

More than one force can be involved in particle assembly, thus assembly templates can guide the assembly in more than one way. Advanced templates combine, for example, a long-range force caused by electrostatic or dielectrophoretic interactions with short-range interactions due to topography that provide high accuracy in the last moments of assembly [6.44]. An electrode array can be created on a flat substrate and a polymer resist patterned on top of the array, so that a hole in the shape of the particle remains. In a similar vein, a hydrophilic substrate can be coated with a hydrophobic resist, which creates a wetting difference that helps to capture a liquid volume in the binding site [6.60].

If one of the particle–template interactions is controllable (as is dielectrophoresis), such templates could

be addressable and certain sites *turned off* during assembly [6.32]. In the style of a raster, a general-purpose master with a relatively dense, regular array of binding sites could then be modulated to produce arbitrary particle arrangements.

The ultimate template would not only be controllable, but could also sense whether a given binding site is occupied, and if so, whether the particle alignment is correct. Together with a feedback loop that controls process parameters, the yield of assembly would then be automatically optimized. This might be easier to realize than it seems: if electrodes are present in a template, it seems feasible to measure the dielectric properties of the binding site, which will likely depend on the presence of a particle (and possibly its alignment).

6.4 Processes and Setups

Particle assembly involves bringing the particles into contact with the targeted surface while avoiding non-specific deposition and agglomeration. If the assembly process takes place on a secondary surface (or interface), an additional process transfers the assembled particles onto the target. This target can then be a structured surface or an entirely plain material, which improves the compatibility of self-assembly with other fabrication methods.

There are only a few specialized setups for assembly, and most researchers use standard laboratory equipment to provide the required conditions. Some classical surface-science equipment can be adapted for assembly, however. The purpose of these setups is to bring surface and particles into contact in a controllable way, where convection and other disturbing influences are minimized, and to monitor and control conditions relevant for the assembly process, such as contact angle, ionic strength, temperature, and field strengths. Excess particles are removed without destroying the particles' order and might be reintroduced to increase the assembly yield. Some setups allow inducing a bias, for example, to align anisotropic particles.

If the assembly takes place at the liquid–solid interface, the final removal of the solvent (if so desired) is a critical step. Capillary forces have frequently been found to destroy or change the particle arrangement. In general, a final quenching of the assembled particles is required to permanently retain their order and enable further processing or integration into a device.

The integration of the assembled particles into a functioning device can involve electrical connections, optical coupling, thermal joining, and many other processing steps. The interfaces that are created often govern the device performance. Surface analysis and modification are therefore common subsequent steps in the integration process.

6.4.1 Setups for Particle Assembly

Langmuir–Blodgett troughs are the classic setup to create monolayers at a gas–liquid interface, and they can be used to assemble particles as well, although the interface naturally only provides a uniform surface as a *template*. Depending on the pressure applied, average particle spacings can be adjusted, which influences the overall properties of the film [6.69].

The gas–liquid interface can also be used to assemble particles in geometrical binding sites, where capillary forces and geometrical confinement at the three-phase boundary line guide the particles. This can either be done in simple immersion setups, where the liquid slowly evaporates and the boundary line moves over the vertically immersed patterned surface, or in more involved setups, for example, the *Capillary Assisted Particle Assembly tool* of *Malaquin* et al. [6.56]. The speed of the moving meniscus, the contact angle, and the hydrodynamic situation inside the liquid (all relevant for the assembly process) are more or less well controlled in the different setups.

Hydrodynamic forces are also used for assembly in the absence of capillary bridges but in the presence of gravity, for larger particles well beyond the limits of *Brownian* behavior, at about one micrometer. In so-called *fluidic assembly*, appropriately shaped objects fall into complementary shaped binding sites from a moving liquid [6.8]. This process is not very efficient, and the objects have to be brought to the surface repeatedly. Setups have been devised to move the object *slurry*, agitate it, and recycle it.

Liquid flows also drive the assembly in *micromolding in capillaries* (MIMIC), a term coined by *Whiteside*'s group [6.70]. In this process, microfluidic channels are filled with particles (usually in densely packed structures). *Xia* introduced a similar method to assemble polystyrene spheres first on flat, but later also

on patterned surfaces: water is drained slowly from his cell through scratches or small ducts at the side, while ultrasonic agitation provides the mobility needed by the particles to arrange themselves [6.71].

Less widespread are vacuum setups for particle deposition. Here, particle production can be coupled to particle assembly and size selection. Particles are first created (usually directly from a metal with thermal methods), separated by size in an electric field, and assembled in a large vacuum chamber [6.25]. While such setups are considerably more complex than most liquid-phase techniques, they allow particles to be deposited on very clean surfaces.

6.4.2 Particle Printing and Processing

It is often desirable to carry out the particle assembly process away from the target substrate. Assembly usually requires binding sites, which might be undesirable to have on the target; it often involves solution chemistry, which might contaminate the target; or it requires specific surface properties, which the target simply might not have. If the particles are assembled on a secondary surface, these requirements are lifted, but a transfer step becomes necessary to bring the particle arrangement to its final destination.

In the classical case of a Langmuir–Blodgett trough, the formed monolayer is transferred by drawing the target surface through the interface vertically (Langmuir–Blodgett films) or by bringing it into contact with the surface horizontally (the Schaefer approach) [6.72]. Alternatively, a stamp is coated with the layer and then prints it onto a target.

Printing has also been demonstrated for single-particle arrays in a process called *self-assembly, transfer, and integration* (SATI), which uses a multistep adhesion cascade [6.73]. In this approach, particles leave one surface in favor of the other due to differences in adhesion, which has to be tuned. The strategy works with particles covering a wide size range; printing of both $100\,\mu m$ and $60\,nm$ particles has been demonstrated [6.59].

Postprocessing of the (printed or directly assembled) particles is generally required if they are to be electrically connected or need to be embedded, protected, or to act either as a template or building block of a further structure. Parallel electric contacting of many assembled nanowires (e.g., for sensing purposes) has been demonstrated using conventional technology on unconventionally assembled particles [6.44]. Other particles have been used as nucleation sites for nanowire growth [6.59], templates for etches and deposition processes, and transistor and memory elements. In all these cases, the particle surfaces were modified or covered by layers of material. A frequent task is the removal of organic adlayers that remain following liquid-phase assembly, which can be effected using plasma ashing or thermal annealing.

6.5 Conclusions

Building devices and materials from nanoparticles has been proven to be a feasible idea. It resembles industrial production from standardized components. The advantages are similar: building blocks, here nanoparticles, can be produced efficiently in large quantities if they are not too complex, and they can be modified and inspected and then used to build different products. As long as it is impossible to build complex structures directly from atoms and molecules, particle assembly will be one of the most interesting routes to creating nanostructures. Templated particle assembly reduced the process complexity even further and existing methods already provide exquisite control over particle positioning.

There are some niches where templated assembly is used industrially today, be it in the fabrication of RFID tags or for bead-based assays, but sub-µm particle assembly is yet to be introduced into production processes. The main challenges here include the typically very large number of particles that require extremely high yields of assembly, the limited quality of even the best chemically synthesized nanoparticles, and the preparation of suitable templates. Once such obstacles are overcome, templated assembly enables hierarchical, complex structures to be made in large quantities using relatively simple equipment.

All these challenges are currently being addressed. Mechanistic understanding of particle synthesis is increasing as synthesis protocols are being analyzed in detail, scale-up is investigated, and alternative routes become available for many popular nanoparticles. An increasing range of particles is now commercially available in consistent quality.

Templates can already be fabricated with high quality on small areas, and various researchers are working on large-scale nanopatterning and replication methods

to produce large areas of identical patterns efficiently. Nanoimprint lithography, for example, can replicate a master many times and is even compatible with *roll-to-roll*-type fabrication, where long plastic sheets are continuously patterned by a rotating drum. As with molding, nanoimprint lithography is not an alternative to templated nanoparticle assembly, since it can only handle a very limited set of materials, but it is ideal for the production of templates.

Finally, the assembly processes themselves are constantly improving. Improved understanding of the interactions during assembly allows researchers to tune the interaction strengths and thereby engineer the energy landscape of the assembly process. Thus, both the stability of the original particles (for example, the colloidal suspension) and their behavior during assembly are optimized towards high yield. In addition, better control of the process parameters during assembly is now possible in modified versions of classical dip-coating setups. When combined with in situ analysis methods, yields and assembly qualities can be optimized by adjusting parameters such as temperature and template velocity.

Today, coatings containing nanoparticles are commonly applied using dip-coating, spin-coating or spray-coating techniques. Such methods are comparatively simple and compatible with a variety of relevant geometries. If templated assembly could be performed using the same deposition techniques, this would render it compatible with established technology and simplify its introduction into other processes. Alternatively, if specialized deposition techniques are required, or if the template cannot be applied to the substrate, assembly can be performed on a specialized template and the particles subsequently transferred onto the target surface. Together, these processes bridge the gap between particle assembly and current standard methods of fabrication. If particles are to be combined with, say, complementary metal–oxide–semiconductor

(CMOS)-type components, the assembly and transfer precision has to be adequate to match the underlying structures. In most cases, short-range accuracy is governed by the assembly process and the precision of the template, while long-range order is influenced mainly by the template and the transfer process. All three may have to be optimized to meet the stringent requirements of semiconductor fabrication.

In addition to such improvements, the development of templated assembly processes for increasingly smaller particles with very high accuracy will continue. An important goal here is the assembly of particles well below 10 nm in diameter, which exhibit electronic quantum effects, with a precision that is sufficient to connect them electronically. Ideally, this would be possible on areas far above the square centimeters that have so far been demonstrated, if possible on standard 300 mm wafers. Finally, the assembly (and, if necessary, the transfer) should be compatible with different particle materials and substrates. A truly versatile process would accept any colloidal particle and thus be able to handle a very wide range of materials including oxides, semiconductors, metals, and polymers, amongst many others.

The ideal process would also handle very small particles. How small? We do not know at present. Gold-55 clusters that resemble molecules rather than particles have already been arranged using templated assembly processes, albeit with a precision far worse than the particle diameter [6.28]. Will it be possible at some point to arrange single atoms and molecules on a surface using a reasonably simple template? That such arrangements are stable and lead to interesting effects has already been demonstrated using high-vacuum scanning tunneling microscopy [6.74]. Whether templated assembly can provide a realistic route to such patterning with ultimate precision will remain an active topic of research for years to come.

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